

References

- BUTT, N. M. & O'CONNOR, D. A. (1967). *Proc. Phys. Soc.* **90**, 247–252.
- BUTT, N. M. & SOLT, G. (1971). *Acta Cryst.* **A27**, 238–243.
- BUYERS, W. J. L. & SMITH, T. (1968). *J. Phys. Chem. Solids*, **29**, 1051–1057.
- LEIBFRIED, G. (1955). *Encyclopaedia of Physics*, Edited by S. FLÜGGE, Vol. VIII/1, p. 197. Berlin: Springer.
- LEIBFRIED, G. & LUDWIG, W. (1961). *Solid State Phys.* **12**, 276–444.
- O'CONNOR, D. A. & BUTT, N. M. (1963). *Phys. Lett.* **7**, 233–235.
- WOLFE, G. A. & GOODMAN, B. (1969). *Phys. Rev.* **178**, 1171–1189.

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On the Application of Phase Relationships to Complex Structures. V. Finding the Solution

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Multiresolution direct methods for solving crystal structures lead to many plausible sets of phases and some means of determining the correct set is necessary. For centrosymmetric structures, figures of merit are usually quite discriminating and the examination of only one or two E maps is necessary. For non-centrosymmetric structures, figures of merit are unreliable and the necessity of examining a large number of E maps can sometime prove to be an almost insuperable obstacle to finding the correct structure. A procedure is described for overcoming this difficulty. The Cooley–Tukey fast-Fourier-transform technique is used to compute E maps and all peaks greater than a certain height are located. A selection of the highest of these peaks, whose number is chosen by the program user, is then analysed with respect to bond lengths and angles. Favourable projections of coherent groups of peaks are output on the line printer in the form of integers representing the ranking order of the peaks and in positions which represent an undistorted projection of the group. Computing time is of the order of one minute per set of phases and the examination of a set of 32 maps and finding the correct solution takes about 30 minutes.

Figures of merit

Some direct methods of solving crystal structures systematically produce a large number of plausible sets of phases (*e.g.* Germain & Woolfson, 1968) but even when a unique solution is sought ambiguities in phase determination are encountered which lead eventually to a multiresolution situation. In such cases it is the normal practice to use various figures of merit to rank the solutions in order of plausibility and then to examine the E maps in ranking order until the correct solution is found.

The correctness, or otherwise, of an E map would be judged by the presence of reasonably related groups of peaks which could be interpreted in terms of the expected chemistry of the material. To examine the three-dimensional E map the usual procedure is to draw contours of sections on sheets of glass or transparent plastic material and to view a stack of the sheets. Even then the interpretation of the map is complicated by the fact that a single molecule or other coherent

structural unit may appear in fragments in various parts of the contoured region.

It is a matter of experience that figures of merit are quite good for indicating the correct set of signs for centrosymmetric structures – normally one need examine no more than two or three maps – but the situation is very much worse with non-centrosymmetric structures. Various figures of merit have been used, for example the ‘absolute figure of merit’ (Germain, Main & Woolfson, 1971), R_{Karle} (Karle & Karle, 1966) and the zero check (Cochran & Douglas, 1957). For particular structures one or other of these may turn out to be more discriminating than the other two but often none of them is reliable and the correct set of phases may be well down in the ranking order.

The automatic interpretation of E maps

With the availability of the Cooley–Tukey fast Fourier transform algorithm it is feasible to compute a large number of E maps – for an average structure and with

five hundred independent reflexions at about one per minute with an IBM 370/155 computer. The output for, say, 32 E maps would be a formidable pile of paper and even to examine six or eight of these represents a Herculean task.

To overcome these practical difficulties we no longer output E maps, but instead examine and interpret the maps within the computer. The various stages of this operation are described below.

(i) An E map is calculated without an E_0 term and is scaled so that all the values at the grid points fall in the range +999 to -999.

(ii) A scan level is set, usually at +100, and all peaks are found which are higher than that level. The positions of the peaks are found by an interpolation process and their coordinates are listed in the computer store.

(iii) The number of peaks to be taken from the list is specified. This number (NPIC) is usually set to a few (5-10) more than the number of atoms to be found which allows for the presence of some spurious peaks. Only the NPIC highest peaks are subsequently considered.

(iv) The interpretation process is now initiated. The distances between all pairs of peaks are found and any

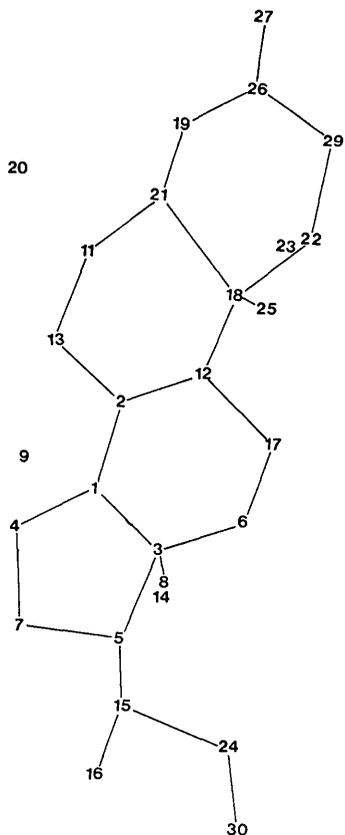


Fig. 1. A representation of the computer output for desoxycorticosterone, $C_{21}H_{30}O_3$, with atomic bonds added.

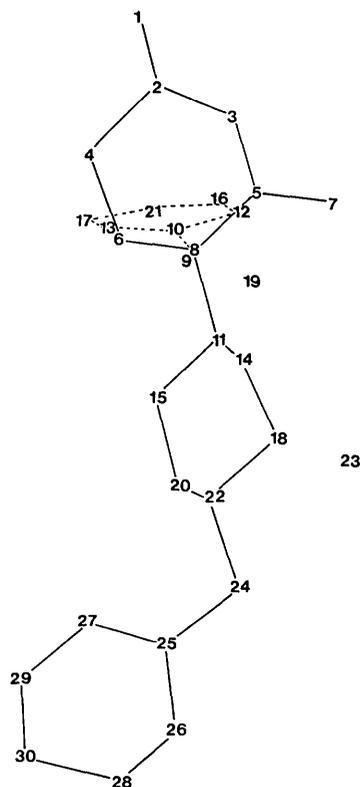


Fig. 2. A representation of the computer output for *levo*-benzimidazole, $C_{23}H_{26}O_2N_2$, with atomic bonds added.

peaks less than a specified distance, d_{max} , apart are recorded as a possible bonded pair of atoms. For an almost-equal-atom organic structure d_{max} may be set at 1.7 Å. By this means one establishes the existence of bonded groups of peaks; there may be only one main group or there may be two or more isolated groups of peaks. A few of the NPIC peaks may not be associated with any group at all. For each group of peaks the bond lengths and bond angles are calculated.

(v) For each fragment found in (iv) a favourable projection direction is sought. Our method of doing this is to find the two peaks the greatest distance apart in the x direction and to find the vector S_1 between them. Then the greatest distance between any two peaks in the y direction is found and also that between any two peaks in the z direction. For the pair of peaks giving the greater of these two distances the vector S_2 between them is found. The projection is made along the direction of $S_1 \wedge S_2$. While other possible ways of projecting are possible this method is easy to apply and gives very satisfactory results. The positions of the peaks are printed as integers on the line printer so as to give a properly scaled view of the projection. Together with this there is printed a list of distances between peaks and also of bond angles.

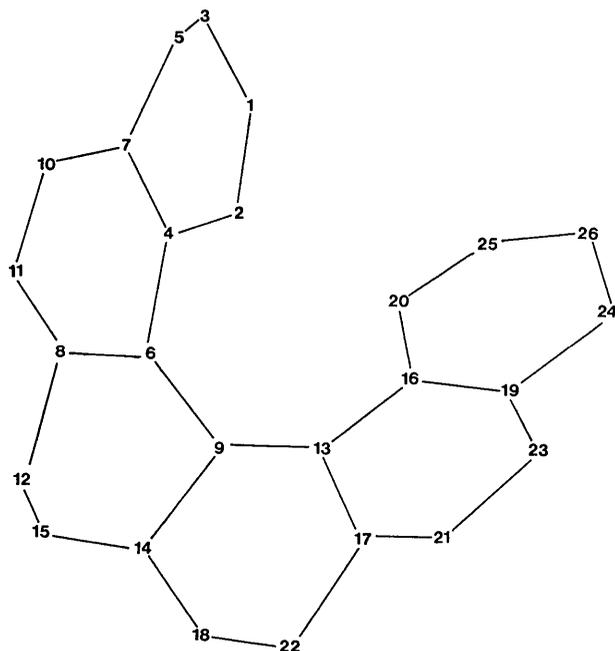


Fig. 3. A representation of the computer output for hexahelicene, $C_{26}H_{16}$, with atomic bonds added.

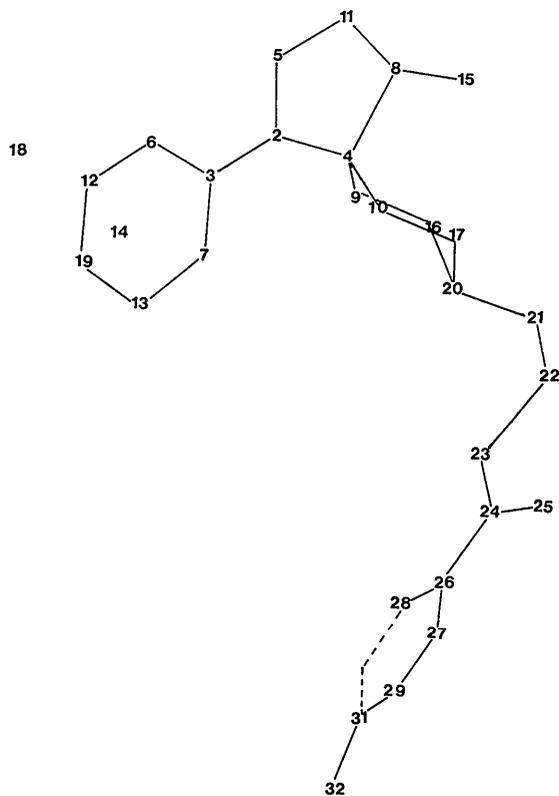


Fig. 4. A representation of the computer output for spiroperidol, $C_{23}H_{26}FN_3O_2$, with atomic bonds added.

With this output information lines can easily be drawn between peak positions and the presence of chemically sensible atomic arrangements is readily detected.

Some examples

1. *Desoxycorticosterone*, $C_{21}H_{30}O_3$, space group $P2_1$ with one molecule in the asymmetric unit

The *MULTAN* system generated 64 sets of phases but examination of these showed that there were only five distinct solutions, the others all being similar to one or other of the five basic ones. These five sets of phases were all examined by the peak-search procedure and the correct solution, shown in Fig. 1, was readily recognized. All the atoms appeared as peaks and six spurious peaks are numbers 9, 14, 23, 10, 20 and 28, the last three of which do not appear since they are disconnected from the others.

2. *levo-Benzidimide*, $C_{23}H_{26}O_2N_2$, space group $C2$ with one molecule in the asymmetric unit

MULTAN generated 32 sets of phases and all these were examined by the peak-search procedure. The correct solution is shown in Fig. 2; peaks 9, 19 and 23 are spurious. On the 'absolute figure of merit' this set of phases ranked 14th, with the zero check it was 17th, and with R_{Karle} , 8th. To have found the correct solution by direct examination of the *E* maps would have been a tedious and very discouraging task in this case.

3. *Hexahelicene*, $C_{26}H_{16}$, space group $P2_12_12_1$ with one molecule in the asymmetric unit

In this case only the three rings corresponding to the lower peak numbers in Fig. 3 were found at the first examination of 32 plots. The phases from these peaks were recycled through the tangent refinement part of the *MULTAN* system and the complete Fig. 3 was then obtained.

4. *Spiroperidol*, $C_{23}H_{26}FN_3O_2$, space group $P2_1/c$ with one molecule in the asymmetric unit

Since it is possible to rely rather more on figures of merit for centrosymmetric structures only one plot was prepared. The plot shown (Fig. 4) corresponded to the highest figure of merit. There were four spurious peaks, numbers 1, 14, 18 and 30 and the atom linking 28 and 31 was missing.

These examples are typical of results from a large number of structures now solved using this technique. Each required of the order of 30 minutes to an hour of computing time to go from raw data to diagrams which revealed the structure in a few minutes of examination.

Conclusions

Virtually all the components of this appendage to the *MULTAN* system are parts of, or modifications of, previously existing programmes of peak search and molecule drawing by computer graphical display. The

novelty in this application is in using these methods as an aid to recognizing structures; normally they are used to represent structures once they have been determined. However we feel that our application is not a trivial one since the examination of masses of *E*-map output had become a major stumbling block in the structure – solving process – especially for non-centrosymmetric structures. Now, on average, 30 minutes of perusal of the graphical displays together with the numerical supplementary information relating to bond lengths and angles is sufficient to find the structure. We have now reached the stage of development where for the vast majority of moderately complex structures no human judgement is required between setting a crystal on an automatic diffractometer to the point of examining the graphical output.

Since they became available some two years ago about 300 structures have been solved by the *LSAM* and *MULTAN* programme packages. The availability of the graphical search routines should make these programmes even more attractive to those who wish to solve moderately complex crystal structures without being too intimately concerned with the method of solution so that it becomes just one more technique for

examining materials albeit a little more complicated than ESR or NMR.

The development of this technique was carried out in the Centre de Calcul, Université de Louvain, and we are grateful for the generous provision of these facilities. We are also grateful to O. Dideberg, L. Dupont, M. Koch, J. P. Putzeys, C. de Rango and G. Tsoucaris for making data available to develop the procedure.

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References

- COCHRAN, W. & DOUGLAS, A. S. (1955). *Proc. Roy. Soc. A* **227**, 486–500.
 GERMAIN, G. & WOOLFSON, M. M. (1968). *Acta Cryst.* **B24**, 91–96.
 GERMAIN, G., MAIN, P. & WOOLFSON, M. M. (1971). *Acta Cryst.* **A27**, 368–376.
 KARLE, J. & KARLE, I. L. (1966). *Acta Cryst.* **21**, 849–859.

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Tessellations and Plane Symmetry Groups as Applied to the Derivation of Closest-Packed Binary Layers

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A method is described for the derivation of binary closest-packed layers of a given composition with the condition that the atoms of the minor component should be crystallographically equivalent. The method is based on the theory of derivatives of space groups developed by Buerger, which is here applied to those multiple cells that may be regarded as tessellations drawn over a basic triangular net. The results are presented for a set of compositions, in order to illustrate the method of derivation.

Introduction

In preceding work concerning the systematic derivation of close-packed structure types (Lima-de-Faria & Figueiredo, 1969), a method was developed in which the rules for derivation followed directly from the conditions for structural stability already discussed (Lima-de-Faria, 1965). Appropriate layers were so deduced for the generation of ordered binary close-packed structures, under the previous statement of crystallographic equivalency for the atoms of the minor component.

The fact that this method applied to the majority of known structures in the area investigated proved its efficacy in deriving the most probable patterns. However, it was not established that all the appropriate layers had been derived. On the other hand, a small proportion were found to have no corresponding appropriate layer; if proved, and not merely a consequence of the simplifications involved in that derivation technique, this circumstance has interesting structural implications. The aim of the present work is to verify these results by applying an exhaustive method to the derivation of these binary close-packed layers.