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Recognition and use of systematically aberrant phase relationships. II.* A simple method.

By Doyle Britton, *Department of Chemistry, University of Minnesota, Minneapolis, MN 55455, USA* and Jack D. Dunitz, *Organic Chemistry Laboratory, Swiss Federal Institute of Technology, ETH-Zentrum, CH-8092 Zürich, Switzerland*

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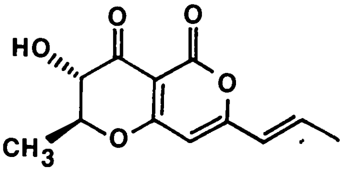
Abstract

Conventional application of direct methods sometimes fails because of systematically aberrant triples. A straightforward method, using unmodified *MULTAN* programs, is given for the solution of such problems. Two successful applications are described.

In a recent paper (Britton & Dunitz, 1981) we gave an example of the solution by direct methods of a structure in which systematically aberrant phase relationships occurred ($S_h S_k S_{h+k} \simeq -1$ rather than $+1$). The solution was based on the procedure described by Theissen & Busing (1974) (henceforth T & B), in which the aberrant triples are identified by comparison of the data set with the Fourier transform of a single benzene ring. We have since been faced with two more examples of the same problem and now have further recommendations on how to solve such structures.

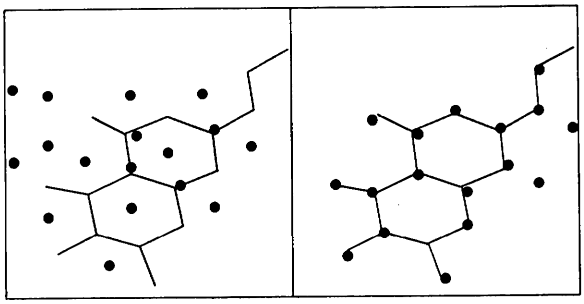


(I)

Radicinin (I), $C_{12}H_{12}O_5$, crystallizes in space group $P2_1$† with $Z = 2$; the salt formed from 1,8-bis(dimethylamino)-naphthalene and picric acid crystallizes in *Pnma* with $Z = 4$. (Complete structures for both will be published elsewhere.) Attempts to solve these structures with *MULTAN* (Main, Woolfson, Lessinger, Germain & Declercq, 1974) gave in each case the characteristic equilateral triangular networks of peaks approximately 1·4 Å apart in the *E* map. The patterns for the *E* maps from the *MULTAN* solution with the largest figure of merit are given in Figs. 1(*a*) and 2(*a*).

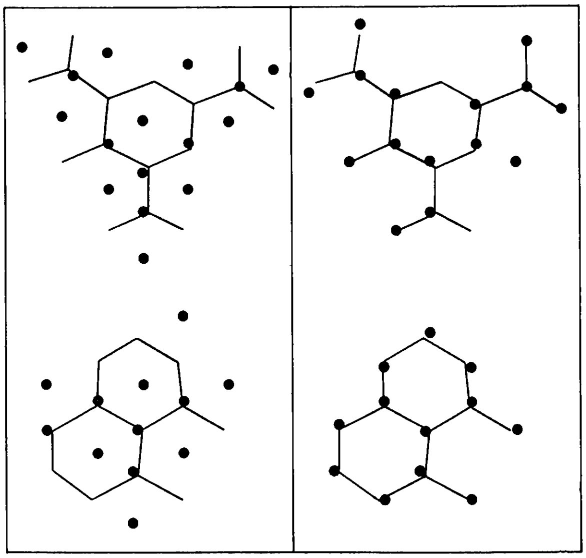
T & B have developed a program to relate the intense reflections to the Fourier transform of benzene. When the orientation of the rings is known, however (as it is once *MULTAN* has been run), it is a simple job to produce a map similar to Fig. 1 in paper I of this series or Fig. 6 in T & B by hand calculation.

Our new approach is based on the following argument: by assuming $S_h S_k S_{h+k} \simeq +1$, *i.e.* by disregarding systematically aberrant triples, *MULTAN* tends to give correct signs to strong reflections lying in the positive region of the



(*a*) (*b*)

Fig. 1. *E* maps for radicinin, $C_{12}H_{12}O_5$. The points show the 17 highest peaks in the *E* maps; the lines show the position of the molecule after solution and refinement of the structure. (*a*) *E* map based on conventional *MULTAN* solution with the best figure of merit. The section at $y = \frac{1}{4}$ is shown. (*b*) *E* map based on phases reassigned as described in the text.



(*a*) (*b*)

Fig. 2. *E* maps for the salt of 1,8-bis(dimethylamino)naphthalene and picric acid, $C_{14}H_{13}N_2^+.C_6H_2N_3O_7^-$. The points show the 28 highest peaks in the *E* map (28 heavy atoms should lie in the mirror plane); the lines show the positions of the ions after solution and refinement of the structure. (*a*) *E* map based on conventional *MULTAN* solution with the best figure of merit. The section at $y = \frac{1}{4}$ is shown. (*b*) *E* map based on phases reassigned as described in the text.

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[*] Part I: Britton & Dunitz (1981).

[†] Although radicinin is optically active, statistical tests indicated a centric or hypercentric structure, and all the peaks in the *E* maps lay close to the plane $y = 0$ (or 1/2). An adequate trial structure could be developed in the higher space group $P2_1/m$. During the refinement, the symmetry was lowered to $P2_1$.

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benzene transform and incorrect signs to those in the negative region. For each of the two new problems the *MULTAN* solution with the highest figure of merit was chosen as a starting point. For reflections lying in the positive region of the benzene transform the phase was taken as found; for reflections lying in the negative region of the benzene transform the phase was changed by 180°. The first 50 reflections on the E list were given fixed phases assigned in this way and another cycle of *MULTAN* was run. The resulting E maps are shown in Figs. 1(*b*) and 2(*b*). In both cases the solutions are essentially correct (15 out of 17 correct peaks in the first case, 26 out of 28 in the second). In both cases this trial structure led to successful refinement.

These two examples suggest that the triangular pattern in the false E map must coincide with the hexagonal pattern in the correct structure in order for this method to work. If the peaks in the false solution were displaced from the correct peaks by something other than a bond vector, as sometimes happens in normal structures even when the figure of merit is large, our procedure would not be expected to lead to the correct solution.

References

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Recognition and use of systematically aberrant phase relationships. I: Erratum.

By DOYLE BRITTON and JACK D. DUNITZ, *Organic Chemistry Laboratory, Swiss Federal Institute of Technology, ETH-Zentrum, CH*-8092 *Zürich, Switzerland*

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Abstract

In the paper by Britton & Dunitz [*Acta Cryst.* (1981), A**37**, 131–132] three errors have been printed. On p. 131, 2nd column, line 5: '–2' should be changed to '–3'; on p. 132, 1st column, line 6: 'one-third' should be changed to 'half'; p. 132, 2nd column, lines 2–3: 'relatively even deeper' should be changed to 'only slightly less deep'.

All the information is given in the *Abstract*.

Notes and News

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ICSD – Inorganic Crystal Structure Data Base

Complementary to the well known Cambridge Crystallographic Data File, a similar file for inorganic substances has been established at the University of Bonn (G. Bergerhoff and I. D. Brown). The current file contains information on 9000 structures: chemical name, chemical formula, mineral name, unit cell, space group, coordinates, temperature factors, references, remarks. More detailed information will be given in a paper to be published in *Acta Crystallographica*. The data base will be made available by Fachinformationszentrum Energie Physik Mathematik GmbH (Dr H. Behrens), D-7514 Eggenstein-Leopoldshafen, Federal Republic of Germany, from 1982 on, in three versions:

1. On-line access *via* telecommunications systems (Euronet, Datex-P, *etc*.).
2. Leasing the up-to-date data base and retrieval programs (IBM-Fortran) at an annual rate.
3. Leasing only the up-to-date data base at an annual rate.

Detailed conditions are available on request from Dr Behrens at the address given above.

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