COX, A. D. & BEAUMONT, J. H. (1980). *Philos. Mag.* B**42**, 115–126.
DAWSON, B. (1967*a*). *Proc. R. Soc. London*, **298**, 255–263.
DAWSON, B. (1967*b*). *Proc. R. Soc. London*, **298**, 264–288.
FALEYEV, N. N., LOMOV, A. A. & LABUSHKIN, V. G. (1981). *Acta Cryst.* A**37**, C374.
FIELD, D. W. (1976). *Phys. Status Solidi A*, **36**, 597–602.
HEALD, S. M. & STERN, E. A. (1977). *Phys. Rev. B*, **16**, 5549–5559.
International Tables for X-ray Crystallography (1952). Vol. I. Birmingham: Kynoch Press.
IVERONOVA, V. I. & REVKEVICH, G. P. (1972) *Teoriya Rasseyaniya Rentgenovskih Luchey* (*Theory of X-ray Scattering*). Moscow: Nauka.
KOLPAKOV, A. V., BUSHUYEV, V. A. & KUZ'MIN, R. N. (1978). *Usp. Fiz. Nauk*, **126**, 479–513.
KORN, G. A. & KORN, T. M. (1968). *Mathematical Handbook*. New York: McGraw-Hill.
PINSKER, Z. G. (1978). *Dynamical Scattering of X-rays in Crystals*. Berlin: Springer.
RENNINGER, M. (1937). *Z. Phys.* **106**, 141–170.
SHUBNIKOV, A. V. & KOPTSIK, V. A. (1972). *Simmetriya v Nauke i Iskusstve* (*Symmetry in Science and Art*). Moscow: Nauka.
TEMPLETON, D. H. & TEMPLETON, L. K. (1980). *Acta Cryst.* A**36**, 237–241.
TEMPLETON, D. H. & TEMPLETON, L. K. (1982). *Acta Cryst.* A**38**, 62–67.
TERMINASOV, Y. S. & TUZOV, L. V. (1964). *Usp. Fiz. Nauk*, **83**, 223–258.
VAINSHTEIN, B. K. (1979). *Sovremennaya Kristallografiya* (*Modern Crystallography*), Vol. I. Moscow: Nauka.

Acta Cryst. (1983). A**39**, 35–37

On the Application of Phase Relationships to Complex Structures. XX. *RANTAN* For Large Structures and Fragment Development

BY YAO JIA-XING*

Department of Physics, University of York, Heslington, York YO1 5DD, England

(*Received* 8 *December* 1981; *accepted* 2 *July* 1982)

Abstract

The *RANTAN* procedure has been used to solve an unknown structure with 100 atoms in the asymmetric unit. In a test of the power of the method a synthetic structure with 234 atoms in space group $P1$ was solved without difficulty. *RANTAN* is also very effective as a multisolution fragment-development procedure with as little as 10% of the structure in the fragment.

Introduction

The *RANTAN* procedure (Yao Jia-xing, 1981) assigns random initial phases to a large number of reflexions together with weights. Subsequent phase refinement is by a controlled use of the tangent formula, in which the weights play a role. *RANTAN* has already been shown to be competitive in power and efficiency with other multisolution methods and further work has now been undertaken to explore the full potentiality of the method and to find new ways of exploiting the general approach.

An unknown structure – complex 2 enniantin C: 1 KSCN

The data for this structure were provided by Dr G. Tischenko of the Institute of Crystallography, Moscow. The basic parameters were: formula $2[(C_{12}H_{21}NO_3)_3]$. KSCN; space group $P2_1$, $Z=2$; $a=20{\cdot}205$, $b=8{\cdot}702$, $c=25{\cdot}587$ Å and $\gamma=97{\cdot}0°$. There were 100 atoms in the asymmetric unit.

MULTAN 80 was tried but did not solve the structure. *RANTAN* employed 400 reflexions ($E>1{\cdot}62$) for the phase-determining process and 100 weak reflexions ($E<0{\cdot}185$) for calculating the PSIZERO figure of merit. The number of strong triple-phase relationships was 4377. The convergence map chose three general reflexions for fixing the origin and enantiomorph. Another 247 reflexions in the bottom of the convergence map were assigned random phases with weights of 0·25 giving a total of 250 reflexions in the starting set.

RANTAN stopped at set 78 automatically and accepted this set as a true solution with figures of merit: ABSFOM 1·0521, PSIZERO 1·149, RESID 18·37, CFOM 2·8822. The E map showed two fragments which contained 40 and 45 atoms respectively. The group KSCN could not be found in the E map, except the carbon atom, since the group was disordered. Fig. 1 shows the molecular structure. The preliminary least-squares refinement was carried out by the *SHELX* 76 program (Sheldrick, 1976) and the R factor was 14·57%. The result showed that the potassium atom had two positions with low occupation factors and that the group SCN seemed to rotate around the heavy centre.

* Permanent address: Institute of Physics, Academia Sinica, Peking, The Peoples' Republic of China.

0567-7394/83/010035-03$01.50

A synthetic structure

In order to investigate the power of *RANTAN* for a somewhat larger structure, a synthetic structure has been tested. Some coordinates were taken from the published structure of valinomycin which contained two independent molecules with space group $P1$ (Karle, 1975). A third molecule was put into an extended unit cell obtained by increasing the b axis from 10·360 to 20·720 Å. All atoms were regarded as carbon atoms, so the crystal data for the synthetic structure were: molecular formula C_{78}; space group $P1$; $Z = 3$; $a = 22{\cdot}285$, $b = 20{\cdot}720$, $c = 14{\cdot}525$ Å, $\alpha = 90{\cdot}06$, $\beta = 105{\cdot}25$, $\gamma = 93{\cdot}31°$; the number of independent atoms was 234.

The structure factors F_c were calculated from these coordinates with an isotropic temperature factor of 4·5 Å^2 and then subjected to random errors with a uniform distribution between ±5% to generate F_o. There were 13 531 reflexions within the resolution of 1·0 Å.

RANTAN was run in the usual way, employing 900 reflexions and 13 345 relationships for phase determination. The random phases with weights of 0·45 were assigned to 350 reflexions in the bottom of convergence map. The best set among 239 trials was set 168 with figures of merit as: ABSFOM 1·0322, PSIZERO 1·383, RESID 18·69, CFOM 2·8557. The E map showed 192 atoms and the remaining atoms were readily obtained from the weighted Fourier technique.

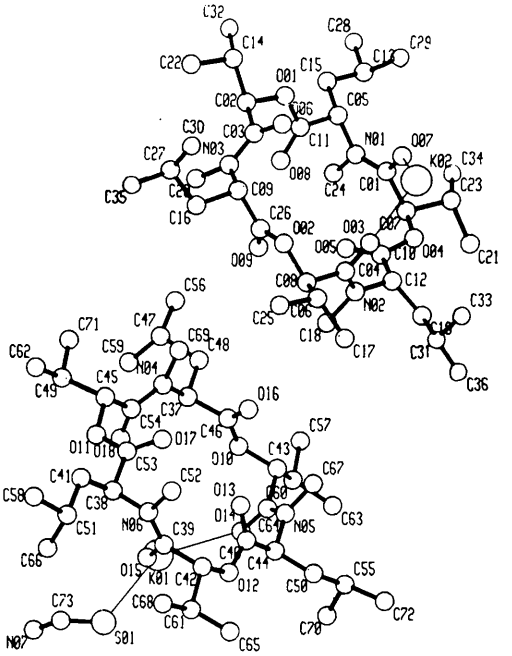

Fig. 1. The molecular structure of ENNI.

Use of partial structure

A number of procedures have been proposed for developing a partial structure into a complete one. One of them is the use of the tangent formula to refine and develop phases obtained from a partial structure (Karle, 1976). Normally the complete structure is obtained by two or more cycles of partial structure development when the partial structure contains 25% or so of the total number of atoms. In fact there are cases when Karle recycling can give a large structure with as little as 5% of the structure in the initial fragment and it is, undoubtedly, a very powerful technique. However, its main disadvantage is that it is not automatic and the process has to be interrupted at the end of each cycle to interpret the latest E map and to find more atoms to include in the next cycle.

In the *RANTAN* approach the partial-structure-derived (PSD) phases are calculated from a fragment and accepted with the same criteria used for Karle recycling as in *MULTAN* 80: (1) $|E_h| \geq 1{\cdot}5$; (2) $|F_h|_{calc} \geq p|F_h|_{obs}$, $(0{\cdot}25 \leq p \leq 0{\cdot}6)$; (3) $W_h \geq 0{\cdot}75$ (Karle, 1976; Main *et al.*, 1980). Since the scattering power of the partial structure is lower and the PSD phase error is likely to be high when the partial structure contains only 10% or less of the total structure, a reduced weight $W_{hr} = 2W_h - 1$ $(W_{hr} \geq 0{\cdot}5)$ is assigned to the PSD phase in the starting set of *RANTAN*. The normal *RANTAN* procedure should be recalled here, that a PSD phase is allowed to change in the refinement process if the new phase is obtained with a weight greater than its initial weight W_{hr}. Two examples of this use of *RANTAN*, which will illustrate the details of its application, are now described.

The first structure was virginiamycin factor-S methanol solvate (Declercq, Germain, Van Meerssche, Hull & Irwin, 1978) which contained 66 independent atoms with space group $P2_12_12_1$. The structure could not be solved in a straightforward way by *MULTAN* or *RANTAN*, but could be solved by using Karle recycling beginning with the positions of 12 atoms. The numbers of atoms in the successive cycles of Karle recycling were 16, 26 and 42. The test was carried out with *RANTAN* by taking six known atoms which generated 25 PSD phases, among which there were three PSD phases having phase error greater than 45°. The other reflexions were assigned random phases with weight of 0·45. *RANTAN* directly found a good solution (set 5) with figures of merit: ABSFOM 1·0393, PSIZERO 1·161, RESID 21·02, CFOM 3·00. The mean phase error of this set was 13° for 300 reflexions and the E map showed a fragment of 52 atoms.

The second example was Ergocalciferol (Hull, Leban, White & Woolfson, 1976) containing 58 individual atoms with space group $P2_12_12_1$. The structure could be solved *ab initio* by *RANTAN* with figures of merit and mean phase error: SET 34,

ABSFOM 0·7814, PSIZERO 2·031, RESID 24·01, MEAN PHASE ERROR 32°. The *E* map showed 45 atoms from which the six highest peaks were taken as a partial structure. There were 59 PSD phases from the partial structure, 13 having a phase error greater than 45°. The number of reflexions was 332 and the usual weights of 0·45 were assigned to other random phases. The subsequent run of *RANTAN* with 100 trials gave the following good-quality solutions:

SET	ABSFOM	PSIZERO	RESID	MEAN PHASE ERROR
31	0·8588	1·723	20·26	15°
34	0·8650	1·682	19·87	14°
38	0·8654	1·708	20·24	15°
45	0·7566	1·891	24·18	22°
72	0·8620	1·685	19·96	15°
79	0·8675	1·650	20·21	15°

Discussion

Recent developments in direct methods, *e.g.* the use of magic integers (Declercq, Germain & Woolfson, 1975) and of random phases (Baggio, Woolfson, Declercq & Germain, 1978) have emphasized the point that it is beneficial to use as many reflexions and relationships as possible in the initial stages of phase development. *RANTAN* represents the most extreme application of this principle and, like the aforementioned methods, it is comparatively insensitive to individual poor relationships. An illustration of this was the solution of the known, but difficult, structure of guaianolide (Posner, Pahiak, Loomis, Frazee, Mittal & Karle, 1981). This structure is characterized by a number of very poorly satisfied relationships, both triplets and quartets, involving large *E*'s and *MULTAN*, which used some of the poor triplets at an early stage, was unable to solve the structure. *RANTAN* solved this structure quite easily giving all but one atom in the first *E* map and it is interesting to note that it could also readily be solved by the magic-integer-based program *MAGEX* (Zhang & Woolfson, 1982).

The use of *RANTAN* in fragment development does introduce a new concept in this field – that of a multisolution approach. The fragment information, used in this way, seems to give one or more solutions corresponding to several cycles of the established methods but with the advantage that it is automatic. Indeed, if some fragment recognition algorithm could be incorporated after *E*-map calculation just to find a few well-related peaks then the whole process could be automated and quite difficult structures solved without user intervention.

I am most grateful to Professor M. M. Woolfson for very helpful discussions and encouragement with this project. My thanks are also due to the Royal Society of London and the Academia Sinica for their support of my stay in the United Kingdom. The help and resources of the University of York Computer Service are also gratefully acknowledged.

References

BAGGIO, R., WOOLFSON, M. M., DECLERCQ, J. P. & GERMAIN, G. (1978). *Acta Cryst.* A**34**, 883–891.

DECLERCQ, J. P., GERMAIN, G., VAN MEERSSCHE, M., HULL, S. E. & IRWIN, M. J. (1978). *Acta Cryst.* B**34**, 3644–3648.

DECLERCQ, J. P., GERMAIN, G. & WOOLFSON, M. M. (1975). *Acta Cryst.* A**31**, 367–372.

HULL, S. E., LEBAN, I., MAIN, P., WHITE, P. S. & WOOLFSON, M. M. (1976). *Acta Cryst.* B**32**, 2374–2381.

KARLE, I. L. (1975). *J. Am. Chem. Soc.* **97**, 4379–4382.

KARLE, J. (1976). In *Crystallographic Computing Techniques*, edited by F. R. AHMED, K. HUML & B. SEDLACEK, pp. 155–164. Copenhagen: Munksgaard.

MAIN, P., FISKE, S. J., HULL, S. E., LESSINGER, L., GERMAIN, G., DECLERCQ, J. P. & WOOLFSON, M. M. (1980). *MULTAN* 80. *A System of Computer Programs for the Automatic Solution of Crystal Structures from X ray Diffraction Data.* Univ. of York, England.

POSNER, G. H., PAHIAK, K. A., LOOMIS, G. L., FRAZEE, W. J., MITTAL, R. A. & KARLE, I. L. (1981). *J. Am. Chem. Soc.* In the press.

SHELDRICK, G. (1976). *SHELX* 76. A program for crystal structure determination. Anorganisch-chemisches Institut der Univ., Gottingen, Federal Republic of Germany.

YAO JIA-XING (1981). *Acta Cryst.* A**37**, 642–644.

ZHANG SHAO-HUI & WOOLFSON, M. M. (1982). *Acta Cryst.* A**38**, 683–685.