unusual features in their molecular structures, isoprene sulphone, thiophen and thiophthen are the only heterocyclic sulphur compounds whose molecular dimensions have hitherto been investigated in detail, and the present requirement seems to be for further structure studies of molecules of a similar type.

Crystallographic data for α-isoprene sulphone

Orthorhombic; $a=10{\cdot}58$, $b=7{\cdot}85$, $c=7{\cdot}68$ A.

$D_m=1{\cdot}37$, $D_X=1{\cdot}375$, $N=4$.

Absent spectra: $(0kl)$ absent for k odd, $(h0l)$ absent for $h+l$ odd.

Space group: *Pbn* or *Pbnm*, probably the former with no molecular symmetry.

I wish to thank Prof. E. G. Cox for his interest and criticism and for the computing facilities available in his laboratories, and Mr Greenhalgh for operating the Hollerith equipment.

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Interpretation of the Patterson Synthesis: Rubidium Benzyl Penicillin

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In substances containing a heavy atom, and suitable multiplicity in the space-group symmetry, the Patterson function may be used directly, by the 'Vector Convergence Method', to give approximate positions of the lighter atoms in the crystal structure. The method is here illustrated by application to the case of rubidium benzyl penicillin. The three-dimensional Patterson function has been calculated and the vectors to the penicillin molecule from the four Rubidium atoms in the unit cell have been studied by construction of 'Vector Convergence Density' maps in three-dimensional space. A fair degree of correlation has been found between these results and the known structure of the crystal.

Introduction

In a recent short communication (Beevers & Robertson, 1950), a technique for interpretation of the three-dimensional Patterson synthesis, the 'Vector Convergence Method', was discussed, and its use in the analysis of the structure of strychnine hydrobromide was mentioned. It was pointed out that the method was applicable when a heavy atom is present, and when the space group confers multiplicity on the crystal structure, e.g. when, as for $P2_12_12_1$, there are four equivalent points in the unit cell.

It is interesting to note the connexions which exist between this method, which arose as a practical expedient in the course of work on an actual structure solution, and the largely theoretical approach which was the subject of a recent paper by Buerger (1950). As was pointed out very clearly in this paper, the Patterson function, or vector set, contains n images of

the n-sided polygon which defines the fundamental set: the actual atomic positions. One may express the argument upon which the vector convergence method is based in this way, that if the Patterson function be placed, correctly oriented, with its origin on a number of the atomic positions successively, the remaining atomic positions will be marked by the convergence of vectors upon them, since, in the process, 'n-gons' in the Patterson function will coincide. When a heavy atom is present in a structure, and its location can be found, and when the multiplicity created by the space-group symmetry is, say, 4, then the Patterson can be placed without difficulty on the four heavy atom positions; the vectors between the heavy atom and the other atoms being of greater weight, facilitate the recognition of atomic positions at the regions of convergence of vectors.

Application of the vector convergence method to rubidium benzyl penicillin

Certain similarities between the strychnine hydrobromide structure and that of rubidium benzyl penicillin (Crowfoot, Bunn, Rogers-Low & Turner-Jones, 1949) suggested that trial of the vector convergence method on the latter might be instructive as well as illustrative of the power of the method in complex structure analysis. It was desirable, in exploration of the powers of the vector convergence method, to study problems similar to that in which some success had already been obtained. The space group was the same and the heavy rubidium atom of almost the same weight as bromine. The structure contained one other atom (sulphur) of weight intermediate between rubidium and carbon; also the rubidium atoms were very nearly on special positions possessing extra symmetry; but it was felt worth while to investigate the applicability of the Patterson method, and to see what difficulties the special features of the case might cause.

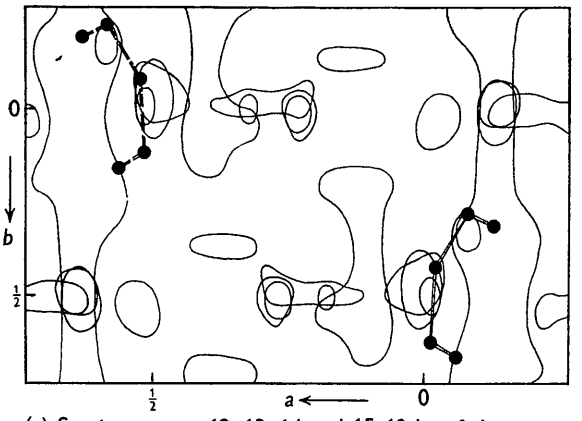
If the heavy atom of a crystal structure is in a general position, then the vector convergence distribution (V.C.D.) has the symmetry of the structure itself only, since in the process of superposition, all the extra symmetry of the Patterson is destroyed. If, however, the heavy atom lies on or nearly on the same level as a screw axis, say, so that pairs of superpositions have nearly identical x, y or z displacements, then an element of the Patterson symmetry enters the V.C.D., which then possesses a mirror plane and has in its unit cell a double number of convergences. This may be explained alternatively as follows: in the derivation of the V.C.D. by n-fold transcription of the Patterson with displaced origin, large numbers of randomly distributed possible atomic positions are obtained, only a fraction, $1/n$, of which coincide at the true atomic positions. Should the heavy atoms be in pairs having almost the same x, y or z parameter, however, vector peaks in the V.C.D., which otherwise would be separate from one another, are brought almost into coincidence and create a set of vector convergences related to the first by mirror-plane symmetry.

In the case of rubidium benzyl penicillin, the fact that the rubidium atoms are very nearly in pairs at $z=0$ and $\frac{1}{2}$, creates mirror planes in the V.C.D. at $z=0$ and $z=\frac{1}{2}$. (Here, and throughout this paper, the co-ordinate system used is the same as that employed by Crowfoot *et al.*) As a result, the quarter-volume of the unit cell between $z=0$ and $\frac{1}{4}$, which should contain convergence peaks corresponding to one molecule only, contains also the mirror image of the adjacent volume between $z=0$ and $-\frac{1}{4}$. The molecules on either side of the plane $z=0$ are related by the screw axis at $z=0$, and $x=\frac{1}{4}, \frac{3}{4}$; hence in the V.C.D. two molecules seem to be present within the planes $z=0$ and $z=\frac{1}{4}$, and appear to be related by glide planes at $x=\frac{1}{4}$ and with translation $\frac{1}{2}b$.

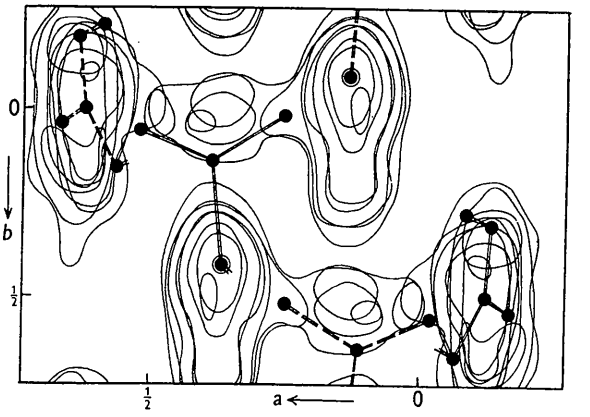
The ambiguity resulting from the duplication of peaks in the V.C.D. would constitute a serious weakness of the method as applied to rubidium benzyl penicillin, were it not possible to overcome it, to some extent at least, by resort to information additional to that relating to the position of the rubidium only. The sulphur atom, whose parameter can be obtained from the V.C.D., is in a general position; if in the three-dimensional Patterson its vectors to the rest of the molecule were to be systematically studied, making allowance for the peaks due to vectors from rubidium, the ambiguity due to the special positions of the rubidium atoms could be resolved. An easier way of taking the sulphur atom position into account, however, is afforded by comparison between the Fourier projections, based on signs derived from rubidium and sulphur structure-factor contributions, and the V.C.D. maps, when certain regions in the latter can be ruled out as highly unlikely for the location of atoms. Combination of the evidence of Fourier projections and the V.C.D. might be sufficient to avoid trial-and-error methods in derivation of the first approximate structure.

Procedure

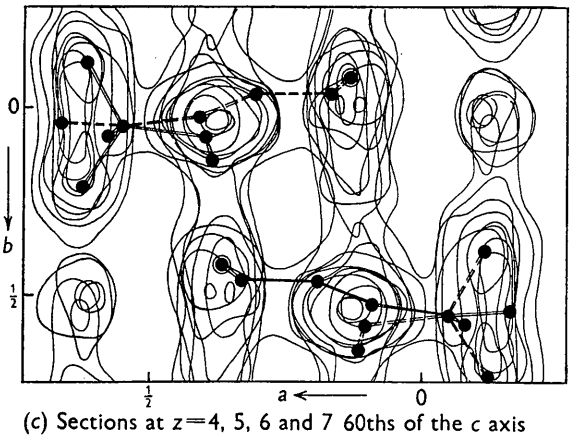
From the observed reflexion intensities obtained by Crowfoot *et al.* (1949), the three-dimensional Patterson synthesis was calculated. For this, the unit cell was subdivided into 15ths along the a and b axes, and into 60ths along the c axis. Then, using the known position of the rubidium atom, the V.C.D. was obtained from the Patterson function. In deriving the V.C.D., only positive values of the Patterson function were considered (the (000) term had been omitted), and the values of the four syntheses were simply added. This was roughly equivalent to taking averages and weighting them according to the number of coincidences of vectors, assuming that positive regions of the Patterson represented the presence of vectors, and negative regions their absence. Contours were then drawn at levels of 'vector convergence density' 25, 100, 150, 200, 500,



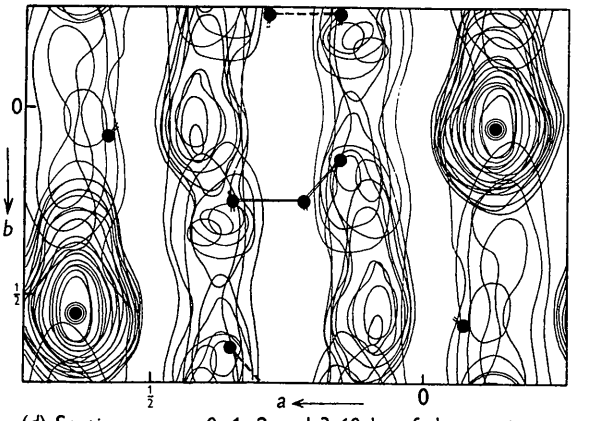
(a) Sections at z=12, 13, 14 and 15 60ths of the c axis



(b) Sections at z=8, 9, 10 and 11 60ths of the c axis

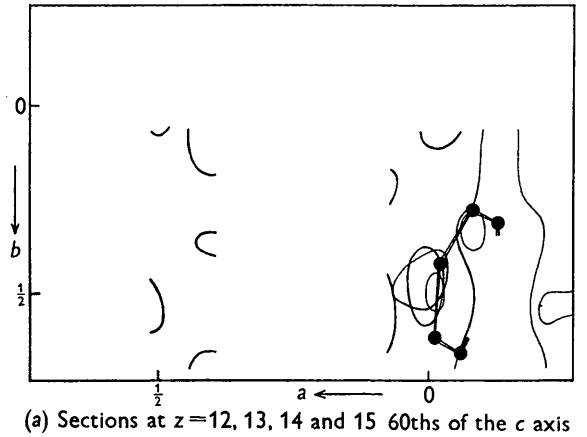


(c) Sections at z=4, 5, 6 and 7 60ths of the c axis

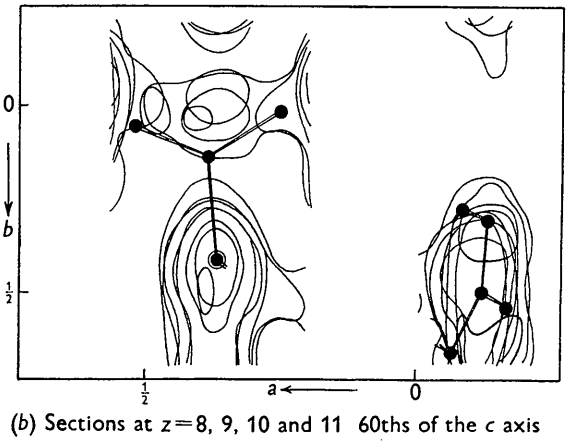


(d) Sections at z=0, 1, 2 and 3 60ths of the c axis

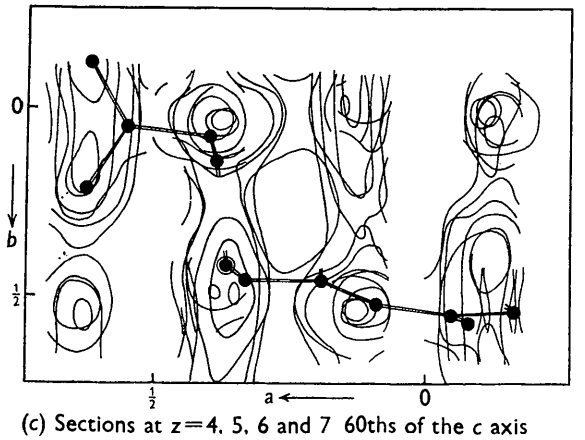
Fig. 1. Vector convergence distribution map.



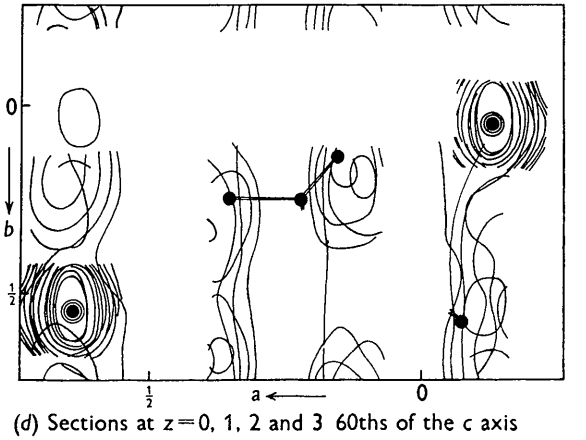
(a) Sections at z=12, 13, 14 and 15 60ths of the c axis



(b) Sections at z=8, 9, 10 and 11 60ths of the c axis



(c) Sections at z=4, 5, 6 and 7 60ths of the c axis



(d) Sections at z=0, 1, 2 and 3 60ths of the c axis

Fig. 2. Vector convergence distribution map with symmetrical peaks erased.

1000 units (the scale of both the Patterson synthesis and the V.C.D. was relative). The sulphur atom reached 250; the rubidium 1400; the carbon, oxygen and nitrogen gave heights of about 50–100 units. Sixteen sections of Fourier space from $z=0$ to $z=15/60$ were used and these were viewed down the z-axis direction looking towards the origin. For the sake of compactness of representation, these sections were taken in four groups of four sections each, the contours for each of the four sections being drawn, superimposed on the other contours, on a single map. The resulting V.C.D. maps are reproduced in Fig. 1 (*a*)–(*d*).

To overcome the ambiguity referred to above, use was made of the Fourier projections which had been calculated by Crowfoot *et al.* (1949, p. 329, Figs. 9 (*a*) and (*b*)) based on signs derived from the contributions of rubidium at $x=0{\cdot}365$, $y=0{\cdot}55$, $z=0$, and sulphur at $x=0{\cdot}625$, $y=0{\cdot}375$, $z=0{\cdot}135$. Regions of the unit cell in which atoms were unlikely, as there were no peaks in the corresponding areas of projection, were marked out. Erasure of the vector convergence peaks in these regions gave the result shown in Fig. 2 (*a*)–(*d*).

Discussion of results

Fig. 3 gives, in projection down the z axis, the positions of the atoms in the quarter-volume of the unit cell of rubidium benzyl penicillin, as found by Crowfoot *et al.* The relevant atomic positions are also indicated in the various sections of Figs. 1 and 2; and in Fig. 1, their duplicates, generated by glide planes at $x=\frac{1}{4}$ and $\frac{3}{4}$, translation $=\frac{1}{2}b$, are also shown, using broken lines for the bond of the second set.

The diagrams show a fair measure of correlation between the structure found by Fourier and trial-and-error methods, and the results of the vector convergence method of Patterson function interpretation, especially as aided by Fourier projections.

How far this general agreement could have been utilized in the initial solution of the structure it is impossible to say. But it would seem that, given the presence of a heavy atom, suitable multiplicity in the space group, and the availability of three-dimensional intensity data, the vector convergence method is likely to be practicable as one further tool in structure determination. Generalization regarding the method is dangerous, considering that its applicability depends upon such a variety of factors. It can only be hoped that continued experiment will prove its real usefulness in crystallographic analysis.

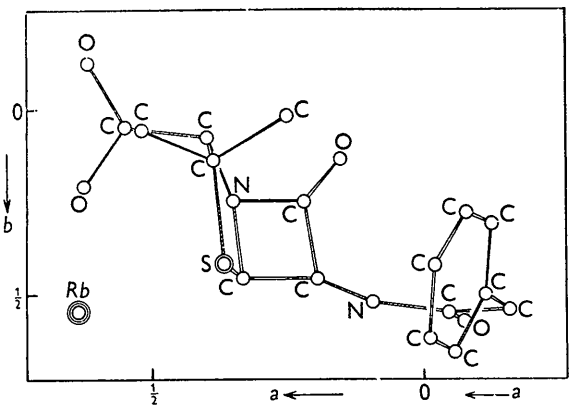


Fig. 3. Rubidium benzyl penicillin: projection down the c axis.

The author wishes to express his thanks to Dr C. A. Beevers, under whose guidance the vector convergence method was originally developed, to Mrs Dorothy Hodgkin, for her interest and encouragement, and to the Carnegie Trust for a scholarship which enabled the work to be carried out. He is also indebted to Mr Stern for a number of helpful suggestions.

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Short Communications

Contributions intended for publication under this heading should be expressly so marked; they should not exceed about 500 words; they should be forwarded in the usual way to the appropriate Co-editor; they will be published as speedily as possible; and proofs will not generally be submitted to authors. Publication will be quicker if the contributions are without illustrations.

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Confirmation of the structure of chromium boride, CrB.

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In a recent paper by Sindeband (1949) the preliminary findings of the structural analysis of CrB conducted by the present author were published. At the same time the structure of this material was being worked on by Dr R. Keissling, and the complete details of his structural analysis have subsequently appeared in print (1949). As