Acta Cryst. (1955). **8**, 195

Applications of the Difference-Patterson Technique in Structure Analysis

By Gopinath Kartha and G. N. Ramachandran

Department of Physics, University of Madras, Guindy, Madras 25, India

(*Received* 27 *September* 1954 *and in revised form* 3 *November* 1954)

The difference-Patterson diagram, obtained by performing a Patterson synthesis with the differences in the intensities of two isomorphous crystals, is very useful for structure analysis, as it contains only peaks at positions corresponding to vectors joining replaceable atoms with other atoms. Methods are described whereby the structure can be deduced from this diagram. All centrosymmetric structures can be solved and among the non-centrosymmetric groups a duplication by an artificial centre of symmetry occurs only in eleven space groups, for general positions of replaceable atom. The method is shown to work with the phthalocyanines and with the isomorphous pair, barium chlorate and barium bromate.

1. Introduction

Buerger (1942) pointed out a simple method of using the X-ray diffraction data of isomorphous crystals for a direct solution of the structure, based on the fact that, in a pair of isomorphous crystals, the nature and positions of the various atoms, other than the replaceable atoms, are comparatively unaffected. Consequently, the Patterson diagrams of the two crystals differ only in so far as the images of the structure, as seen from the replaceable atoms, are concerned. Therefore, if one plots a new function whose value at any point is the difference in the two Patterson functions, then the new diagram will contain only images of the crystal structure, as seen from the various replaceable atoms and their inverses. We may call this the Difference-Patterson diagram (D-P diagram). Obviously, the peaks in the D-P diagram correspond to the atomic position in the crystal structure if there is only one replaceable atom per unit cell and the structure has a centre of symmetry.

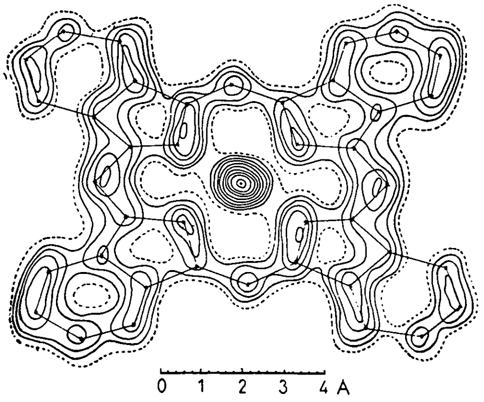

Fig. 1. Difference-Patterson projection along the *b* axis of the phthalocyanine molecule, calculated from the data for nickel and free phthalocyanines. The atomic positions determined by Robertson (1936) are shown by crosses. Note the absence of the plane of symmetry in the projected molecule. Only a small number of contours are drawn because the D-P function was calculated only at a coarse interval of 10°.

Although the above idea was put forward nearly twelve years ago, it does not appear to have been applied so far in practice. Recently, the authors had the occasion to calculate the D-P projection of the phthalocyanines along the *b* axis, using the data for nickel and free phthalocyanines (Robertson, 1936). The diagram (Fig. 1) exhibits remarkable agreement with the positions of atoms as determined by Robertson, using the phase method. This suggested that the D-P method should be explored further. The reason why it has not been put to use so far is probably that there will be much overlap in the D-P projection if the number of replaceable atoms is more than one; the phthalocyanines happened to be a happy choice for trying out the method. However, the situation is quite different if one examines the three-dimensional D-P diagram. Here the number of peaks is only of the order of the number of atoms (n) in the crystal structure itself (multiplied by a factor of 2 or 4 perhaps), but it is very much less than the number of peaks in the simple Patterson (n^2). A study has been made of the possibilities of the three-dimensional D-P diagram and the main results are given in the succeeding sections. It is shown that, making use of Buerger's minimum-function method (Buerger, 1951), the crystal structure can be recovered from the D-P diagram in a vast majority of space groups (including many non-centrosymmetric ones), provided the replaceable atom is in a general position. Even if the atoms are in special positions, the technique would work in many cases, but sometimes the structure is duplicated by additional symmetry elements.

2. General results*

Let p be the number of replaceable atoms in the unit cell denoted by $a_1, a_2, \ldots, a_p$ (type A), and np the

---

* The proofs of the various statements made in this section are omitted to conserve space. A part of these results has been stated by Buerger (1942), but they have also been included here for the sake of completeness and continuity.

total number of atoms. The non-replaceable atoms may be denoted by $b_1, b_2, \ldots, b_p$ (type B), $c_1, c_2, \ldots, c_p$ (type C), etc. We may indicate the peaks in the Patterson function by specifying the two interacting atoms, the first symbol representing the atom from which the Patterson vector originates and the second the atom at which it terminates, e.g. (a_1b_2). The set of vectors from one atom to all atoms of one type may be represented by symbols of the type (a_1B), while the set of vectors from all atoms of one type to all atoms of another type is represented by a symbol such as (AB). Clearly, we have $(a_ib_j) = -(b_ja_i)$ and similarly $(AB) = -(BA)$. Then, it can be shown that in the D-P diagram the relative weights of the peaks corresponding to interactions of the type $\pm(AB)$, $\pm(AC), \ldots$ are proportional to the weights (scattering powers) of the atoms of type B, C respectively, while the relative weight of type (AA) is increased in the ratio $(1+\alpha):1$, where α is the ratio of the scattering powers of the replaceable atoms in the two isomorphous crystals. Thus, the D-P diagram contains $2p$ images of the crystal structure, all of the same weight, with the modification that the weight of the replaceable atom alone is different from that in the original structure.

Now suppose that the vectors between the replaceable atoms are known, i.e. the set (AA) is known; the methods for determining these are described in § 3. Then, if the set of replaceable atoms (supposed to be point atoms) has no centre of inversion, the original structure can be recovered from the D-P diagram. For this the D-P diagram is given a translation equal to the translation (a_ia_j) and one picks out the peaks which superpose with the undisplaced diagram. The process is repeated, choosing all the values of j from 1 to p. Then the set of peaks at which p-fold coincidences occur give uniquely the image of the crystal structure as seen from atom a_1. In the case of the D-P diagram of a real crystal in which the atoms have finite radii, one makes use of Buerger's minimum-function method (1951) by drawing contours corresponding to the lower of the two values of the Patterson function in the two superposed diagrams. Since the atoms a_1–a_p are equivalent, and therefore have the same weight, it is unnecessary to multiply the Patterson function by any factor for obtaining the minimum function.

It may be mentioned that the minimum-function method is superior to the method suggested by Rogers (1951), which is effectively what might be termed a sum-function method similar to the vector-convergence method of Beevers & Robertson (1950). The defect in both these methods is that the non-superposed peaks lead to a large background.

It can also be shown that if the configuration of replaceable atoms (supposed to be point atoms) has a centre of inversion, while the structure as a whole has no centre of symmetry, then (and only then) a duplication of the original structure occurs by inversion about this point. Corollaries of this are:

(a) If $p = 1$ and the structure has no centre of symmetry, there is always duplication by inversion.
(b) If $p = 2$, the two replaceable atoms automatically have a centre of inversion midway between them and so the structure is duplicated by inversion about this point, if it is not centrosymmetric.
(c) If $p > 2$ and the replaceable atoms occupy general positions, a duplication by an artificial centre of symmetry occurs only in the space groups $P4$, $I4$, $P6$.

The full list of space groups in which such a duplication occurs when the replaceable atoms are in general positions is:

$$P1,\ P2,\ P2_1,\ C2,\ Pm,\ Pc,\ Cm,\ Cc,\ P4,\ I4,\ P6\ .$$

Thus, in a vast majority of cases, the problem of solving the crystal structure consists only of calculating the three-dimensional D-P function and then performing purely geometrical operations on it.

3. Use of replaceable groups instead of replaceable atoms

The duplication mentioned above which occurs with non-centrosymmetric crystals arises because the set of replaceable atoms may have a centre of symmetry even though the structure as a whole does not. When $p = 1$ or 2, this condition is true not only with point atoms but also with spherically symmetric atoms. Similarly, for $p > 2$ also, a set of spherically symmetric atoms has a centre of symmetry if the configuration of their centres has this symmetry. Since the electron-density distributions in atoms have practically spherical symmetry, it is obvious that a duplication of the real structure would arise under the above conditions even if the atoms are of finite size, and not point atoms.

However, if the replaceable part of the structure is not a single atom (or set of equivalent atoms) but a group of atoms which does not have a centre of inversion (such as CO_3, SO_4 or COOH), then this difficulty does not arise. In such a case the original structure should be capable of being recovered by choosing suitable translations (corresponding to the vectors joining the different atoms in the group) for plotting the minimum function. This method should work even if $p = 1$ and the structure has no symmetry whatever. However, it would be necessary in such a case to weight the D-P function suitably before translating it so as to allow for the differences in the scattering powers of the various atoms in the group. Thus it should be possible to work out the atomic positions in any crystal structure, provided a pair of isomorphous crystals can be obtained with suitable substituents.

4. Finding the positions of replaceable atoms

The problem of obtaining the correct structure from the D-P requires a knowledge of the positions of the replaceable atoms. In this section, we shall consider the methods to be used for this purpose.

Since the peaks in the D-P diagram occur only at positions corresponding to the vectors from *replaceable atoms* to the rest of the structure, the Harker sections of the D-P diagram will contain only the replaceable-atom Harker interactions.* The accidental non-Harker peaks, if any, which occur in the section can only be those in which one of the interacting atoms is the replaceable atom. Consequently, the confusion due to non-Harker background (which usually occurs owing to accidental coincidences in the simple Patterson diagram of a complicated crystal structure) is very much reduced in the D-P. The Harker peaks will also be small in number since all the Harker interactions between non-replaceable atoms are suppressed, and so all the peaks, both Harker and non-Harker, are likely to be well resolved.

The problem therefore reduces to finding which of the peaks in the Harker sections are real, and which are accidental. The considerations advanced by Buerger (1946) in connection with the 'implication diagram' are very useful for this purpose. If the symmetry elements of the crystal structure contain a screw axis or a glide plane (symmetries which are associated with a translation), then the accidental coincidences may be recognized by comparing two parallel Patterson sections, one corresponding to the translation demanded by the symmetry element and the other through the origin. The former section would contain peaks due to both Harker and non-Harker peaks. Further details about this are not given here. It is found that with a two-fold screw axis this method does not work if there is only one other atom accidentally at the same level as the replaceable atom (it works if there are two or more such non-replaceable atoms). Even in such a case, an examination of a general pair of sections parallel to the Harker section separated by a distance corresponding to the two sections mentioned above would be sufficient to find the true Harker peaks. If none of the symmetry elements has a translation associated with it, then a comparison of a section through the origin and any other parallel to it (containing a few peaks) will be sufficient to pick out the Harker peaks in the former.

The above procedures do not require any special computations or drawings, for the first step in the application of the present method would be the determination of the three-dimensional D-P function. The data thus obtained would contain all the sections mentioned in the previous paragraph and it is only necessary to compare the difference sections and make the proper interpretations.

The number of peaks found in any section would be small (of the order of the number of atoms in a section of the structure itself), since only interactions between replaceable atoms and the rest of the structure occur in the D-P. Because of this, we could determine the height, contrast and shape of each peak occurring in a Harker section. This information could also be utilized for distinguishing the Harker peaks from the non-Harker peaks. A true Harker peak will be spherical, whereas, unless the coincidence is exact, a non-Harker peak will not have true spherical symmetry near the Harker section. Now, the height of the Harker peaks for any atom a is given by

$$P_a \propto \int \varrho_a^2 dv \propto \int_0^\infty \xi^2 f^2(\xi) d\xi$$

(Kartha, 1953) and these values which are characteristic of the atom at a given temperature could be calculated for different atoms. The proportionality constant is the same for all atoms in a given structure. Thus knowledge of peak height, shape and contrast would in most cases enable one to distinguish the Harker peaks from non-Harker interactions and thus fix the positions of the replaceable atoms.

5. Examples of the application of the D-P method

The example of the phthalocyanines has already been mentioned. The method has also been applied to the isomorphous crystals of barium chlorate and barium bromate. These crystals belong to the space group $I2/a$ with $p = 8$ and their structure has been studied in detail (Kartha, 1952). The D-P gives the vectors between the replaceable halogen atoms and the rest of the structure, together with their inversions. Since the halogen positions are known, the three-dimensional D-P function could be combined to give actual atomic

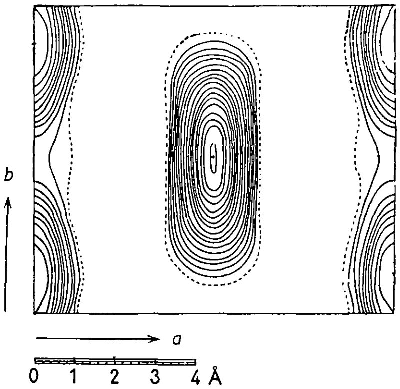

Fig. 2. Difference-Patterson projection along the c axis obtained from the data for barium chlorate and barium bromate. The crosses indicate the positions of the barium and halogen atoms. Note the extra plane of symmetry perpendicular to the b axis.

---

* Buerger (1942) has pointed this out in principle.

positions in the structure without any ambiguity. However, in the D-P projection along the c axis (Fig. 2) extra peaks occur in addition to the correct ones marked by crosses. These are due to the fact that the replaceable halogen atoms have coordinates very near $x = 0{\cdot}25$, $y = 0{\cdot}25$. This accidental position, not demanded by the symmetry of the crystal, introduces a mirror of reflexion perpendicular to the b axis in the D-P projection.

The same difficulty occurs even if we use Robertson's phase method. The contribution of replaceable atoms is zero for half the total number of reflexions in this zone, and hence their phases cannot be determined by that method. This lack of knowledge introduces an additional symmetry element in the computed distribution, a symmetry not already present in the structure.

The difficulty found in solving a non-centrosymmetric structure when the replaceable set of atoms has a centre of symmetry may be illustrated with reference to rubidium benzyl penicillin, which was discussed by Robertson (1951) in connection with the vector-convergence technique using the heavy-atom method. The most prominent of the peaks in the Patterson diagram are due to vectors from the rubidium atom to other atoms. Although the space group of the compound is $P2_12_12_1$, the set of rubidium atoms possess a reflexion plane, because they occur in pairs close to $z = 0$ and $z = \frac{1}{2}$. Consequently, the final structure obtained by the vector-convergence method contains also a duplicate of the real structure obtained by a reflexion in the plane.

The D-P method is likely to prove useful for the pair of isomorphous crystals, haemoglobin and its compound with mercury, which have been recently used by Perutz to find the phases of the various reflexions (Bragg, 1954). Since the projection on the b plane has a centre of symmetry, one could take all the observed reflexions into account and draw the D-P, utilizing all the observed data, instead of only the low-angle reflexions, as has been done for calculating the electron-density distribution in Fig. 2 of the above reference. However, in the three-dimensional diagram an additional centre of symmetry will be introduced since $p = 2$ for these crystals. This difficulty could be overcome if two different atoms could be introduced into the haemoglobin structure, or if an asymmetric group could be introduced instead of the mercury atom.

6. Comparison with the usual procedure for isomorphous crystals*

The experimental data required for the usual method of determining the signs (or phases) of isomorphous crystals are the same as those required for the present method. It is therefore worthwhile to compare the relative advantages of the two methods.

In the phase method we assume that the positions of the replaceable atoms are known, in which case we know the contribution due to those atoms alone for any reflexion. Then, if we denote by $F = P+iQ$ the structure amplitude of the first crystal and by $F' = (P+iQ)+(p+iq)$ that of the second crystal, where $(p+iq)$ is the additional contribution due to the change of the replaceable atom, then P and Q can be determined, knowing $|F|^2$, $|F'|^2$, p and q. This determination, except in a singular case, gives an ambiguous result for the phase of F, since it requires the solution of a quadratic equation.

If the structure does not have centrosymmetry, but the set of replaceable atoms has this symmetry, then the above ambiguity is equivalent to a duplication of structure by an artificial centre of symmetry.

In the absence of any criterion for distinguishing between the two solutions, the best that can be done is to perform a Fourier synthesis, using *both* solutions, when the resulting structure will have an extra centre of symmetry located at the inversion centre of replaceable atoms alone (see, for example, Bokhoven, Schoone & Bijvoet, 1951). This situation is identical with the D-P method.

However, the calculation of the phase for each reflection is a laborious problem and becomes very inaccurate if the contribution due to the replaceable atoms is zero or very small. A similar difficulty arises also with Rogers' method, where reflexions for which the contribution from the replaceable atom is small have to be dropped out of the summation. On the other hand this difficulty is not present in the D-P method. Here all the observed X-ray diffraction data could be utilized in calculating the first approximation to the structure. The calculations are also much simpler in the D-P method.

However, if the set of replaceable atoms also has no centre of symmetry, then the phase method practically fails. In this case, the phases of the two solutions are symmetrical about the phase $p+iq$ and it is difficult to give a meaning to the structure obtained by taking both solutions into account. However, it is precisely in this case that the D-P method is fully applicable. By making use of the minimum function method with the difference-Patterson diagram the structure can be unambiguously solved. It is interesting to note that in all the structures so far solved by the phase method, the replaceable atoms did have a centre of symmetry.

Finding the positions of the replaceable atom is a difficult problem in the phase method, unless the replaceable atom in one of the crystals is of large atomic number. In the D-P, on the other hand, the replaceable atom can be readily located owing to the relatively smaller number of peaks occurring in its Harker sections.

In conclusion, it may be said that, although the D-P method is probably not very useful with projections, the interpretation of the three-dimensional D-P dia-

---

* Part of the discussion in this section was clarified as a result of an interesting comment of Prof. Ewald.

gram in terms of the crystal structure is in general possible. In view of this, it may be worth while obtaining the three-dimensional data required for this purpose, using a suitable pair of isomorphous crystals. Most of the structures which are of interest at present are concerned with organic compounds, and with these compounds one often finds that the introduction of an extra group in the molecule does not change the type of crystal structure. In such cases, by making a judicious choice of the extra group, the D-P method could be utilized to obtain full information regarding the structure of the whole molecule. Thus it appears that the D-P method deserves more attention as a practical means for structure analysis than it has had so far.

References

Beevers, C. A. & Robertson, J. H. (1950). *Acta Cryst.* **3**, 164.
Bokhoven, C., Schoone, J. C. & Bijvoet, J. M. (1951). *Acta Cryst.* **4**, 275.
Bragg, W. L. (1954). *Nature, Lond.* **174**, 55.
Buerger, M. J. (1942). *Proc. Nat. Acad. Sci. Wash.* **28**, 281.
Buerger, M. J. (1946). *J. Appl. Phys.* **17**, 579.
Buerger, M. J. (1951). *Acta Cryst.* **4**, 531.
Kartha, G. (1952). *Proc. Indian Acad. Sci.* A, **36**, 501.
Kartha, G. (1953). *Acta Cryst.* **6**, 817.
Robertson, J. H. (1951). *Acta Cryst.* **4**, 63.
Robertson, J. M. (1936). *J. Chem. Soc.* p. 1195.
Rogers, D. (1951). *Research*, **4**, 295.

Acta Cryst. (1955). **8**, 199

The Crystal Structure of Dimethylphosphinoborine Trimer*

By Walter C. Hamilton†

Gates and Crellin Laboratories of Chemistry, California Institute of Technology, Pasadena 4, California, U.S.A.

(*Received* 22 *July* 1954)

Dimethylphosphinoborine trimer, $[(CH_3)_2PBH_2]_3$, is orthorhombic, with $a = 11{\cdot}16 \pm 0{\cdot}02$, $b = 13{\cdot}16 \pm 0{\cdot}02$, $c = 10{\cdot}53 \pm 0{\cdot}02$ Å, $Z = 4$, and space group *Pnma*. The intensities of the 1210 planes with $\sin\theta \leq 0{\cdot}886$ were visually estimated from equi-inclination Cu $K\alpha$ Weissenberg photographs. The approximate structure was derived from a three-dimensional Patterson synthesis, and refinement in three dimensions was carried out by successive least squares and by use of a difference map. A simple method was used for estimating approximate temperature factors from the difference map. The molecule has a cyclohexane-like ring of alternating P and B atoms, with two methyl groups attached to each P, and two hydrogens to each B. It has crystallographic symmetry C_s and approximate symmetry C_{3v}, and the immediate environment of each ring atom is approximately C_{2v}. The average bond lengths and angles (and estimated standard deviations) are P–B, $1{\cdot}93_5 \pm 0{\cdot}009$; P–C, $1{\cdot}83_7 \pm 0{\cdot}007$ Å; P–B–P, $112{\cdot}2 \pm 0{\cdot}9$; B–P–B, $118{\cdot}1 \pm 1{\cdot}2$; C–P–C, $100{\cdot}4 \pm 0{\cdot}6$; B–P–C, $109{\cdot}1 \pm 0{\cdot}6°$. The R factor for the final structure is 0·169.

Introduction

Dimethylphosphinoborine trimer, $[(CH_3)_2PBH_2]_3$, made from dimethyl phosphine and diborane, has been described as being the most stable well-defined compound containing a B–H bond yet prepared (Burg & Wagner, 1953). It is extraordinarily stable toward both hydrolysis and thermal decomposition. Burg has postulated that the structure is a hexatomic ring with six equivalent P–B bonds, and that the resistance toward hydrolysis is primarily due to special characteristics of the bonding rather than to steric hindrance by the methyl groups, which, however, he says, might be of some importance. It seemed of interest to attempt a complete crystal-structure determination of this unusual compound in order to confirm the ring structure and to attempt to elucidate the nature of the bonding. Stosick had previously determined the cell constants of the orthorhombic unit cell (Burg & Wagner, 1953).

Experimental

Both needle- and plate-like crystals, 0·2–0·3 mm. in maximum dimension in the a and c directions and as much as 1 mm. in the direction of the needle axis b, were used for the diffraction photographs. To prevent rapid sublimation, it was found necessary to mount the crystals in glass capillaries for all X-ray work.

From rotation and Weissenberg photographs about the a and b axes and precession photographs about three axes, using Cu $K\alpha$ ($\lambda = 1{\cdot}542$ Å) and Mo $K\alpha$ ($\lambda = 0{\cdot}711$ Å) radiation, the cell constants were found to be

---

* Contribution No. 1924 from the Gates and Crellin Laboratories.

† Allied Chemical and Dye Corporation Predoctoral Fellow, 1953–54. Present address: The Mathematical Institute, 10 Parks Road, Oxford, England.