

# AN APPLICATION OF THE DIFFERENCE-PATTERSON METHOD

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Received March 14, 1956

(Communicated by Prof. G. N. Ramachandran, F.A.Sc.)

## 1. INTRODUCTION

As early as 1942, Buerger (1942) has pointed out that the Difference-Patterson or the Difference-implication diagram could be used to find the positions of atoms in structure. Donnay and Buerger (1950) have computed the Difference-implication map to get the positions of Mg and Fe atoms in the structure of tourmaline. An extension of the Difference-Patterson (D-P) was applied by Frueh (1953) to facilitate the solution of order-disorder problems in minerals. Again, Buerger (1953) has suggested that an application of the minimum function method to the D-P maps could help in solving the crystal structure.

In a recent paper, Kartha and Ramachandran (1955) have shown that the D-P method can be systematically and successfully applied to analyse crystal structures. The present paper is mainly concerned with an attempt to apply the method to a more complicated example, namely, the isomorphous crystals di-*p*-tolyl telluride and di-*p*-tolyl selenide, whose structures have been worked out by Blackmore and Abrahams (1955 *a, b*). In their report, complete data are given of all the measured structure factors and these could be utilised to calculate the D-P diagram. The two compounds crystallise in the orthorhombic system, space group  $P2_12_12_1$ , with four molecules per unit cell. The unit cell dimensions are:

Selenide:  $a = 25.12 \text{ \AA}$ ;  $b = 7.99 \text{ \AA}$ ;  $c = 5.88 \text{ \AA}$ .

Telluride:  $a = 25.33 \text{ \AA}$ ;  $b = 8.05 \text{ \AA}$ ;  $c = 6.01 \text{ \AA}$ .

## 2. THE D-P DIAGRAM OF THE *b* PROJECTION

The electron density projections given by them showed that the *b*-axis projection was free of overlap and so it was first tried. Using the data of  $F(h0l)$ ,  $|F(h0l)|^2$  were calculated for the two crystals and the Patterson function was computed in each case. The Patterson function of the selenide was subtracted from that of the telluride and the difference was plotted. The resulting D-P diagram is shown in Fig. 1.

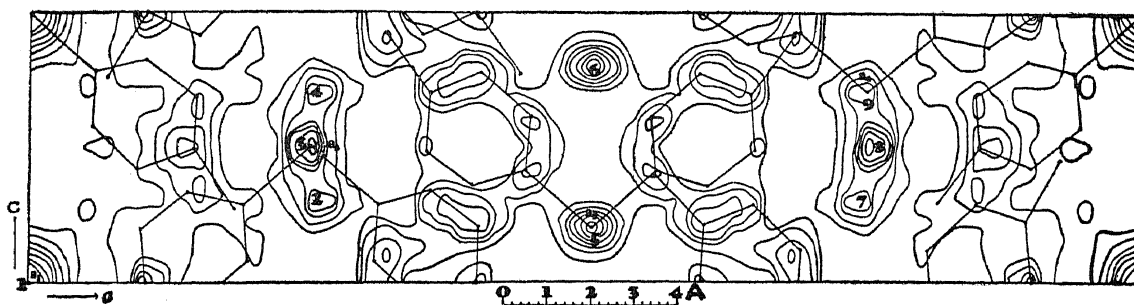


FIG. 1. The D-P projection of di-*p*-tolyl telluride and selenide along the *b*-axis. Contours for the heavy atom peaks are at intervals five times as much as the intervals of contours for other peaks.

The D-P diagram should contain only peaks at the termini of vectors joining the replaceable atoms (Te or Se) with themselves or the other atoms in the structure. The strong peaks, corresponding to the vectors joining the replaceable atoms only, occur in the diagram at the positions: (1) 0, 0; (2) 0.25, 0.30; (3) 0.25, 0.50; (4) 0.25, 0.70; (5) 0.50, 0.20; (6) 0.50, 0.80; (7) 0.75, 0.30; (8) 0.75, 0.50; (9) 0.75, 0.70. Of these, peaks 2, 4, 7 and 9 are of nearly the same strength while 3, 5, 6 and 8 are of double the strength, while peak 1 at the origin is four times as strong. The positions of the replaceable atoms could be obtained from the D-P diagram by translating it so as to make one of the peaks (*e.g.*, 2) coincide with the origin and marking out the positions of the peaks which superpose (the theory of this is simple). Since the structure has a centre of symmetry in the projection, this straightaway gives the positions of the replaceable atoms, namely 1, 3, 5 and 9. These are designated by  $a_1$ ,  $a_2$ ,  $a_3$  and  $a_4$  (Fig. 1).

In order to get the positions of the other atoms, the D-P diagram was then given a translation equal to  $(a_2 a_1)$ ,  $(a_3 a_1)$  and  $(a_4 a_1)$  so as to bring each of the other peaks in coincidence with the peak  $a_1$  and the positions of the peaks which superpose were marked in each case. Owing to diffraction effects some of the fainter peaks were suppressed or displaced if they occurred near a strong peak in the D-P diagram. Consequently an average was taken of all the measurements. The molecule thus determined is shown associated with each of the replaceable atoms in Fig. 1.

In finding the superposition it must be remembered that in the D-P diagram a certain peak will be doubled or quadrupled, according to the replaceable atom peak with which it is associated. A certain amount of judgment is therefore needed in finding the superposed positions.

## 3. COMPARISON WITH EXACT STRUCTURE

The fractional co-ordinates of the atoms in the molecule with respect to the heavy atom are listed in Table I, together with the exact values for

TABLE I

Atoms	D-P method		Electron density method			
	<i>x</i>	<i>z</i>	Telluride		Selenide	
			<i>x'</i>	<i>z'</i>	<i>x''</i>	<i>z''</i>
C <sub>1</sub>	-0.060	0.217	-0.0614	0.2161	-0.0604	0.1918
C <sub>2</sub>	-0.056	0.408	-0.0545	0.4133	-0.0551	0.3972
C <sub>3</sub>	-0.100	0.600	-0.0961	0.5602	-0.0994	0.5367
C <sub>4</sub>	-0.148	0.500	-0.1458	0.5144	-0.1484	0.4700
C <sub>5</sub>	-0.150	0.292	-0.1528	0.3160	-0.1539	0.2649
C <sub>6</sub>	-0.100	0.175	-0.1108	0.1691	-0.1097	0.1262
C <sub>7</sub>	-0.190	0.733	-0.1913	0.6733	-0.1955	0.6187
C <sub>1'</sub>	+0.060	0.217	+0.0637	0.2128	+0.0602	0.2020
C <sub>2'</sub>	+0.056	0.408	+0.0637	0.3960	+0.0558	0.4098
C <sub>3'</sub>	+0.100	0.600	+0.1074	0.5428	+0.1002	0.5540
C <sub>4'</sub>	+0.148	0.500	+0.1503	0.5016	+0.1481	0.4894
C <sub>5'</sub>	+0.150	0.292	+0.1503	0.3201	+0.1516	0.2833
C <sub>6'</sub>	+0.100	0.175	+0.1074	0.1732	+0.1077	0.1391
C <sub>7'</sub>	+0.190	0.733	+0.1975	0.6583	+0.1957	0.6459

the telluride and selenide structures as determined by Blackmore and Abrahams (1955 *a, b*). It will be noticed that the agreement is fairly good except for the methyl carbon atoms C<sub>7</sub> and C<sub>7'</sub> for which the *z* co-ordinates are appreciably different. This is due to the diffraction effect of the strong peaks. In all the eight positions, this particular atom is displaced roughly in the same way so that the displacement is not evened out by averaging.

Another point worthy of note is that the molecule as determined from the D-P diagram is symmetric about a line parallel to the *c*-axis. This symmetry is really absent, but in the superposition method of finding the peaks the differences noticed were not considered significant and an average was struck between the two halves of the molecule.

Further it must be mentioned that the Se and Te atoms are not exactly in the same positions in the two crystals. In fact a typical Te-Te vector has the components 0.26, 0.28 (as determined from the corresponding simple Patterson function) while the corresponding Se-Se vector is 0.26, 0.22 and in the D-P diagram the corresponding peak occurs at 0.25, 0.30 which is to be expected. So it is interesting to note that the D-P diagram has quite

sharp peaks corresponding to the replaceable atom interactions, in spite of the relative displacement of the corresponding atoms in the two isomorphous crystals and that the weaker peaks corresponding to the other interactions are also well defined. This shows that the D-P method can be confidently applied in general to isomorphous crystals even though the replaceable atoms may slightly differ in their positions.

#### 4. APPLICATION OF VECTOR SET METHOD TO THE PATTERSON DIAGRAM

During the preparation of the Difference-Patterson diagram, it was observed that there was a close correspondence between the peaks in it and the peaks found in the ordinary Patterson diagram of the selenide and the telluride. This is to be expected because both Se and Te atoms are so much larger scatterers than the carbon atoms that the C-C interaction will be of small intensity compared to the Te- or Se-C and Te-Te or Se-Se interactions. Consequently the methods described in the previous section was applied directly to the Patterson projection of di-*p*-tolyl selenide along the *b*-axis. But for a background due to the C-C peaks which is seen from the fact that the minimum value of the Patterson function is nearly 2,000, as compared with value close to zero of the D-P map, this diagram is not inferior to the D-P diagram. However, there is the advantage that the shift and a small broadening of the peaks, which is present in the D-P diagram due to the difference in the positions of the atoms in the two crystals, is absent here.

Table II gives the co-ordinates of the atoms in one molecule obtained from it. The deviation  $\Delta'$  from the exact value are shown in the table and may be compared with the deviations  $\Delta$  found with the structure deduced from the D-P. It will be observed that the deviations are small and more or less the same but for the deviations in the position of the methyl carbon atoms, which are fairly large in both cases.

In order to test the usefulness of the method, the R value was calculated with the co-ordinates in Table II and was found to be 0.36 taking all the reflexions observed by Blackmore and Abrahams (1955 *b*) in this zone. It may be mentioned that taking the co-ordinates from the telluride structure unchanged the above authors found an R value of 0.45. Thus the simple Patterson could have been used directly to get an even better first approximation by the application of vector set method. In fact if it is assumed that the methyl carbon atom is in line with the two benzene ring carbon atoms, which are in the *para* positions relative to each other, then the mean deviation would be even less.

The same method was applied to the Patterson projection of di-*p*-tolyl selenide along the *c*-axis. The projection is shown in Fig. 2. As before

TABLE II

Atoms	D-P method			Electron Density			Image method			Deviation in Å			Deviation in Å		
	$x_1$	$z_1$	$x_2$	$z_2$	$x_3$	$z_3$	$\Delta x = x_1 - x_2$	$\Delta z = z_1 - z_2$	$\Delta x' = x_3 - x_2$	$\Delta z' = z_3 - z_2$	$\Delta x = x_1 - x_2$	$\Delta z = z_1 - z_2$	$\Delta x' = x_3 - x_2$	$\Delta z' = z_3 - z_2$	
Se	..	..	0.136	0.138	0.133	0.139	..	..	..	..	..	..	-0.075	0.006	
C <sub>1</sub>	0.073	0.356	0.075	0.330	0.071	0.339	-0.050	0.156	-0.100	0.054	-0.100	0.054	-0.100	0.054	
C <sub>2</sub>	0.077	0.547	0.081	0.535	0.065	0.572	-0.100	0.072	-0.375	0.222	-0.375	0.222	-0.375	0.222	
C <sub>3</sub>	0.033	0.719	0.037	0.675	0.033	0.656	-0.100	0.264	-0.100	-0.114	-0.100	-0.114	-0.100	-0.114	
C <sub>4</sub>	0.985	0.639	0.988	0.608	0.983	0.606	-0.075	0.186	-0.125	-0.012	-0.125	-0.012	-0.125	-0.012	
C <sub>5</sub>	0.983	0.431	0.982	0.403	0.973	0.422	0.025	0.168	-0.225	0.014	-0.225	0.014	-0.225	0.014	
C <sub>6</sub>	0.330	0.314	0.026	0.264	0.025	0.289	0.175	0.300	-0.025	0.150	-0.025	0.150	-0.025	0.150	
C <sub>7</sub>	0.943	0.872	0.941	0.757	0.961	0.839	0.050	0.690	0.500	0.492	0.500	0.492	0.500	0.492	
C <sub>1</sub> '	0.193	0.356	0.196	0.340	0.195	0.339	-0.075	0.096	-0.025	-0.006	-0.025	-0.006	-0.025	-0.006	
C <sub>2</sub> '	0.189	0.547	0.192	0.548	0.201	0.572	-0.075	-0.006	0.225	0.144	-0.075	0.144	0.225	0.144	
C <sub>3</sub> '	0.233	0.719	0.236	0.692	0.233	0.656	-0.075	0.162	-0.075	-0.156	-0.075	-0.156	-0.075	-0.156	
C <sub>4</sub> '	0.281	0.639	0.284	0.628	0.283	0.606	-0.075	0.066	-0.025	-0.132	-0.075	-0.132	-0.025	-0.132	
C <sub>5</sub> '	0.283	0.431	0.288	0.421	0.291	0.422	-0.125	0.060	0.075	0.006	-0.125	0.075	0.075	0.006	
C <sub>6</sub> '	0.233	0.314	0.244	0.277	0.243	0.289	-0.275	0.222	-0.025	0.132	-0.275	0.222	-0.025	0.132	
C <sub>7</sub> '	0.323	0.872	0.332	0.784	0.305	0.839	-0.225	0.528	-0.675	0.330	-0.225	0.528	-0.675	0.330	

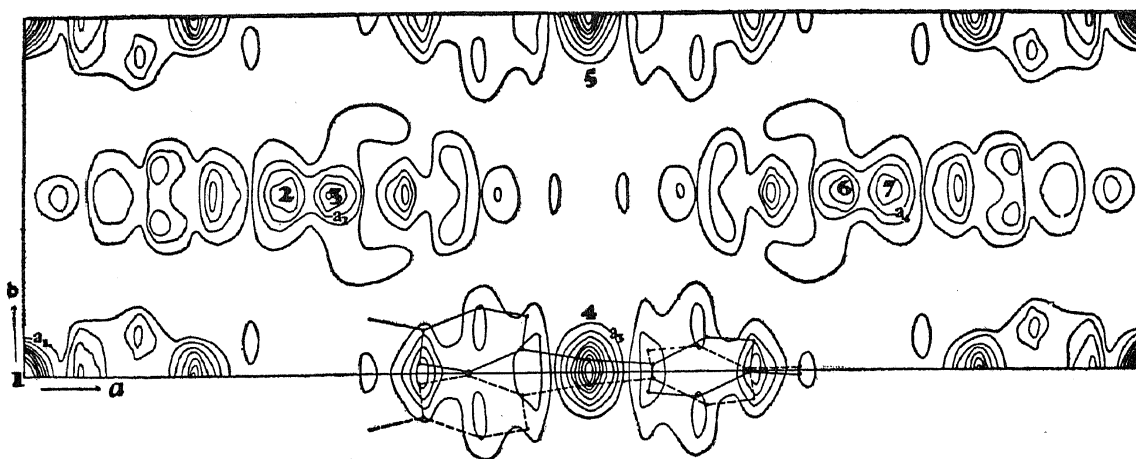


FIG. 2. The Patterson projection of di-*p*-tolyl selenide along the *c*-axis. Contour intervals are as in Fig. 1.

the strong peaks are designated by numbers from 1 to 7, and the positions of the replaceable atoms by  $a_1$ ,  $a_2$ ,  $a_3$  and  $a_4$ . The *y* co-ordinate thus obtained is very close to 0.25. Because the *y* co-ordinate is close to  $\frac{1}{4}$  every replaceable atom peak is doubled and further the rest of the molecule associated with the two peaks are related by a reflection on the *b*-plane. Hence it is difficult to uniquely interpret the diagram. The two possible positions of the molecule associated with one of the strong peaks are shown in figure. However if the presence of a benzene ring is previously known, a rough idea of the disposition of the molecule can be got. This projection is therefore more difficult to interpret than the previous one. It is thus seen that the interpretation of the heavy atom diagram or the D-P diagram may become difficult if the heavy atom or replaceable atom has special values for the parameters.

Thus, in general, it is clear that Buerger's idea of solving the Patterson map directly for the crystal structures can be profitably applied if there is a heavy atom and if there is no appreciable overlap in the projection. In the present case the structure had a centre of symmetry in the projection and no doubling of structure was introduced. If such a symmetry is not present, then the structure can be uniquely solved if (a) the number of replaceable atom peaks is greater than two, and (b) the group of replaceable atoms do not have a centre of symmetry (Kartha and Ramachandran, 1955).

The D-P technique is being systematically applied for solving unknown crystal structures in this laboratory.

In conclusion, the author wishes to express his sincere gratitude to Professor G. N. Ramachandran, for the keen interest he took in this study.

## SUMMARY

The Difference-Patterson (D-P) technique is applied to a complicated example, namely, the isomorphous crystals, di-*p*-tolyl telluride and di-*p*-tolyl selenide, whose structures have been recently reported. It is shown that the D-P method can be confidently applied in general to isomorphous crystals, even though the replaceable atoms may slightly differ in their positions. Also, Buerger's vector set method is applied to the Patterson projections of the di-*p*-tolyl selenide along *b*- and *c*-axes. It is shown that Buerger's method can be profitably used when there is no appreciable overlap in the projection and if the heavy atoms or the replaceable atoms do not have special values for their parameters.

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