

Table 4. (cont.)

Unobserved reflexions

hkl	F_o	F_c	hkl	F_o	F_c	hkl	F_o	F_c	hkl	F_o	F_c
26,0,0	<3.9	-0.2	32,0,2	<3.5	+0.3	105	<3.9	-1.9	507	<2.0	-0.4
30,0,0	<3.9	-1.6	34,0,2	<3.1	+0.6	305	<3.9	+0.4	307	<2.1	0
34,0,0	<3.3	-0.6	36,0,2	<2.2	+0.6	11,0,5	<3.9	+0.8	107	<2.1	+0.3
38,0,0	<2.2	+0.3	35,0,3	<2.2	-0.3	13,0,5	<3.8	-0.1	107	<2.0	+0.5
39,0,1	<1.5	+0.1	31,0,3	<3.0	+0.7	17,0,5	<3.6	-1.1	507	<1.8	+0.4
35,0,1	<3.1	-0.8	29,0,3	<3.5	+1.2	18,0,6	<2.8	+0.5	710	<4	3
29,0,1	<3.9	-0.4	27,0,3	<3.8	+1.3	16,0,6	<3.0	+0.8	910	<4	1
25,0,1	<3.9	+2.3	23,0,3	<3.9	-0.2	14,0,6	<3.2	+0.8	14,1,0	<5	5
21,0,1	<3.5	+3.3	21,0,3	<3.8	-1.6	12,0,6	<3.3	+0.4	22,1,0	<5	4
19,0,1	<3.2	+1.5	17,0,3	<3.6	-3.3	10,0,6	<3.4	-0.2	24,1,0	<5	7
9,0,1	<2.1	-5.1	13,0,3	<3.3	-0.1	606	<3.5	-1.1	920	<4	8
31,0,1	<3.8	-0.9	11,0,3	<3.2	+3.0	406	<3.5	-1.1	10,2,0	<5	4
33,0,1	<3.3	-0.1	13,0,3	<3.4	+4.3	206	<3.6	-0.6	12,2,0	<5	9
35,0,1	<3.0	+0.4	14,0,4	<3.9	+1.0	006	<3.6	+0.1	17,2,0	<5	0
37,0,1	<2.3	+0.6	18,0,4	<3.9	-1.4	206	<3.5	+0.7	330	<5	6
38,0,2	<1.6	-0.4	17,0,5	<3.9	+1.3	406	<3.5	+1.1	630	<5	8
36,0,2	<2.2	-0.7	13,0,5	<3.9	+1.7	606	<3.4	+1.0	730	<5	1
28,0,2	<3.9	+1.3	11,0,5	<3.9	+1.5	10,0,6	<3.3	0	830	<5	6
26,0,2	<3.9	+2.1	905	<3.9	+0.7	12,0,6	<3.1	-0.5	930	<5	9
22,0,2	<3.7	+1.3	705	<3.9	-0.6	14,0,6	<2.9	-0.7	11,3,0	<5	6
802	<2.5	-6.1	505	<3.9	-1.7	16,0,6	<2.5	-0.7	12,3,0	<5	0
30,0,2	<3.7	-0.3	305	<3.9	-2.2	18,0,6	<2.0	-0.4			

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A Unified Program for Phase Determination, Type 4P

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The unified program for phase determination, valid for all the space groups and both the equal and unequal atom cases, is completed here for all the centrosymmetric space groups. The present paper is concerned with the space groups comprising type 4P, which is characterized by the noteworthy fact that the value of no phase may be arbitrarily specified, once the functional form for the structure factor has been chosen. A detailed procedure for phase determination is described.

1. Introduction

This is the seventh in a series of papers concerned with a program for phase determination initiated by us (Karle & Hauptman, 1959, hereafter referred to as 1P). With this paper, the application of the new probability methods, based on the Miller indices as

random variables, is completed for the ninety-two centrosymmetric space groups. We are here concerned with the four space groups comprising Type 4P (Hauptman & Karle, 1959), *Im3*, *Ia3*, *Im3m* and *Ia3d* of the cubic system. Although these space groups are conventionally body-centered, they are referred, in

this paper, to the primitive unit cell defined in our paper on the seminvariants (Hauptman & Karle, 1959). Also listed in the latter paper is a set of coordinates for each space group. This is equivalent to choosing the functional form for the structure factor which is employed here. We present a detailed procedure for phase determination which utilizes the same general formula and, at the same time, makes use of relationships among the structure factors characteristic of each space group.

2. Notation

The same notation as appears in 1P (1959) is employed here.

3. Phase determining formulas

3.1. Basic formulas

$$B_{2,0}: \mathcal{E}'_{\mathbf{h}}{}^2 = 1 + \frac{4\pi\sigma_2^2}{2^{(p+q+2)/2} p q \Gamma\left(\frac{p+1}{2}\right) \Gamma\left(\frac{q+1}{2}\right) \sigma_4} \times \langle \lambda_{p\mathbf{k}} \lambda_{q(\mathbf{h}+\mathbf{k})} \rangle_{\mathbf{k}} + R_{2,0}. \quad (3.1.1)$$

$$B_{3,0}: \mathcal{E}'_{\mathbf{h}_1} \mathcal{E}'_{\mathbf{h}_2} \mathcal{E}'_{\mathbf{h}_1+\mathbf{h}_2} = \frac{(2\pi)^{3/2} \sigma_2^3}{2^{(p+q+r+3)/2} p q r \Gamma\left(\frac{p+1}{2}\right) \Gamma\left(\frac{q+1}{2}\right) \Gamma\left(\frac{r+1}{2}\right) \sigma_4^{3/2}} \times \langle \lambda_{p\mathbf{k}} \lambda_{q(\mathbf{h}_1+\mathbf{k})} \lambda_{r(\mathbf{h}_1+\mathbf{h}_2+\mathbf{k})} \rangle_{\mathbf{k}} - 2 \frac{\sigma_6}{\sigma_4^{3/2}} + \frac{\sigma_8^{1/2}}{\sigma_4} (\mathcal{E}'_{\mathbf{h}_1} \mathcal{E}'_{\mathbf{h}_1}{}'''' + \mathcal{E}'_{\mathbf{h}_2} \mathcal{E}'_{\mathbf{h}_2}{}'''' + \mathcal{E}'_{\mathbf{h}_1+\mathbf{h}_2} \mathcal{E}'_{\mathbf{h}_1+\mathbf{h}_2}{}'''') + R_{3,0}. \quad (3.1.2)$$

3.2. Integrated formulas

$$I_{2,0}: \mathcal{E}'_{\mathbf{h}}{}^2 = 1 + \frac{2\sigma_2^2}{C_1^2(t)\sigma_4} \langle A_{t\mathbf{k}} A_{t(\mathbf{h}+\mathbf{k})} \rangle_{\mathbf{k}} + R_{2,0}'. \quad (3.2.1)$$

$$I_{3,0}: \mathcal{E}'_{\mathbf{h}_1} \mathcal{E}'_{\mathbf{h}_2} \mathcal{E}'_{\mathbf{h}_1+\mathbf{h}_2} = \frac{\sigma_2^3}{C_1^3(t)\sigma_4^{3/2}} \langle A_{t\mathbf{k}} A_{t(\mathbf{h}_1+\mathbf{k})} A_{t(\mathbf{h}_1+\mathbf{h}_2+\mathbf{k})} \rangle_{\mathbf{k}} - 2 \frac{\sigma_6}{\sigma_4^{3/2}} + \frac{\sigma_8^{1/2}}{\sigma_4} (\mathcal{E}'_{\mathbf{h}_1} \mathcal{E}'_{\mathbf{h}_1}{}'''' + \mathcal{E}'_{\mathbf{h}_2} \mathcal{E}'_{\mathbf{h}_2}{}'''' + \mathcal{E}'_{\mathbf{h}_1+\mathbf{h}_2} \mathcal{E}'_{\mathbf{h}_1+\mathbf{h}_2}{}'''') + R_{3,0}'. \quad (3.2.2)$$

In these formulas, p, q, r and t are restricted to be positive. Ordinarily they are given values in the range 2-4.

The remainder terms are given in the appendix § 6 and in 1P (1959). Equation (3.1.1) or (3.2.1) serves to determine the magnitudes of the structure factors $|\mathcal{E}'_{\mathbf{h}}|$ corresponding to the squared structure. By means of equation (3.1.2) or (3.2.2), the phases of these structure factors $\varphi'_{\mathbf{h}}$ may be determined. In the next section we describe in detail how these equations are to be used for the various space groups included in type 4P.

4. Phase determining procedure

It is assumed that the $|\mathcal{E}'_{\mathbf{h}}|$ have been calculated from the observed intensities. From these, the $|\mathcal{E}'_{\mathbf{h}}|$ are obtained by applying (3.1.1) or (3.1.2). In fact it may be advantageous to compute the $|\mathcal{E}'_{\mathbf{h}}|$ over a range of reflections extending beyond that of the original set of observations. We are here concerned only with the larger $|\mathcal{E}'_{\mathbf{h}}|$, and it is the phases of these whose values are to be determined. In the application of (3.1.2) or (3.2.2), the values of some $|\mathcal{E}'_{\mathbf{h}}{}''''|$ may be required. These may be estimated from the corresponding $|\mathcal{E}'_{\mathbf{h}}|$ or $|\mathcal{E}'_{\mathbf{h}}{}''|$, or calculated from (3.1.1) or (3.2.1) in which \mathcal{E} is replaced by \mathcal{E}' and \mathcal{E}'' by \mathcal{E}''''' , given sufficient data.

In the phase determining procedures to be described,

Table 1

The coefficients of $\mathcal{E}'_{\mathbf{h}_1} \mathcal{E}'_{\mathbf{h}_2}$ given by the left side of (3.1.2) or (3.2.2), for selected values of \mathbf{h}_1 and \mathbf{h}_2 and for each of four space groups of type 4P. Each column may undergo cyclic permutation. The notation $P(Im3)$ refers to the primitive unit cell, instead of the conventionally centered one (cf. Hauptman & Karle, 1959)

\mathbf{h}_1	$h_1, k_1, h+\bar{k}_1$	$h_1, \frac{1}{2}(h+k+2\bar{h}_1), \frac{1}{2}(h+\bar{k}+2\bar{h}_1)$	$h_1, \bar{h}+h_1, \bar{h}+\bar{k}+h_1$
\mathbf{h}_2	$\bar{h}+\bar{h}_1, h+\bar{k}_1, k_1$	$h+\bar{h}_1, \frac{1}{2}(\bar{h}+k+2h_1), \frac{1}{2}(\bar{h}+\bar{k}+2h_1)$	$h+\bar{h}_1, h+k+\bar{h}_1, \bar{h}_1$
$\mathbf{h}=\mathbf{h}_1+\mathbf{h}_2$	\bar{h}, h, h	\bar{h}, k, \bar{k}	$h, k, \bar{h}+\bar{k}$
		$h \equiv k \pmod{2}$	
$P(Im3)$	+1	+1	+1
$P(Im3m)$			
$P(Ia3)$	$(-1)^{h_1+k_1}$	$(-1)^{\frac{1}{2}(h+k)}$	+1
$P(Ia3d)$			
\mathbf{h}_1	$\frac{1}{2}(h+\bar{k}+l), \frac{1}{2}(h+k+l), \frac{1}{2}(\bar{h}+k+l)$	$\frac{1}{2}\bar{k}+l, \frac{1}{2}k, h+\frac{1}{2}k+l$	$\frac{1}{2}(2h+l+\bar{k}_1), k_1, \frac{1}{2}(\bar{h}+l+\bar{k}_1)$
\mathbf{h}_2	$\frac{1}{2}(h+k+l), \frac{1}{2}(\bar{h}+k+l), \frac{1}{2}(h+\bar{k}+l)$	$h+\frac{1}{2}k+l, \frac{1}{2}k, \bar{h}+\frac{1}{2}\bar{k}$	$\frac{1}{2}(h+l+k_1), \bar{k}_1, \frac{1}{2}(h+2l+k_1)$
$\mathbf{h}=\mathbf{h}_1+\mathbf{h}_2$	h, k, l	h, k, l	$h, 0, l$
	$h+k+l \equiv 0 \pmod{2}$	$k \equiv 0 \pmod{2}$	$k_1 \equiv \bar{h}+l \pmod{3}$
$P(Im3)$			
$P(Im3m)$	+1	+1	+1
$P(Ia3)$			
$P(Ia3d)$	+1	$(=1)^l$	$(-1)^l$

Table 2

For $Im\bar{3}m$ and $Ia\bar{3}d$, the coefficients of $\mathcal{E}'_{\mathbf{h}_1}$ given by the left side of (3.1.2) or (3.2.2), for selected values of \mathbf{h}_1 and \mathbf{h}_2 . Each column may undergo cyclic permutation

\mathbf{h}_1	$h_1, l + \bar{k}_1 + 2\bar{l}_1, l_1$	$h_1, h + \bar{l}_1, l_1$	$h_1, k, \bar{k} + \bar{l}$	$h_1, \bar{h} + \bar{l} + h_1, l + \bar{l}_1$	$\frac{1}{4}(3\bar{k} + k + 2l), \frac{1}{4}(\bar{l} + k + 2\bar{l}), \frac{1}{4}(\bar{h} + k + 2l)$
\mathbf{h}_2	$\bar{h}_1, \bar{l} + h_1 + 2l_1, l + \bar{l}_1$	$h + \bar{h}_1, \bar{h}_1, l_1$	$h + \bar{h}_1, h_1, l$	$h_1, \bar{h} + \bar{l}_1, l + \bar{l}_1$	$\frac{1}{4}(h + \bar{k} + 2l), \frac{1}{4}(\bar{h} + 3k + 2l), \frac{1}{4}(h + \bar{k} + 2l)$
$\mathbf{h} = \mathbf{h}_1 + \mathbf{h}_2$	$0, 0, l$	$h, \bar{h}, 0$	$h, 2k, 2\bar{k} + 2\bar{l}$	h, \bar{h}, l	h, k, l
$P(Im\bar{3}m)$	$+1$	$+1$	$+1$	$+1$	$h - k \equiv 2l \pmod{4}$
$P(Ia\bar{3}d)$	$(-1)^{h_1}$	$(-1)^{h+l_1}$	$(-1)^k$	$(-1)^{h_1+l}$	$(-1)^{\frac{1}{4}(h-k+2l)}$

it will be seen that the first steps concern the application of (3.1.2) or (3.2.2) with choices of indices which take full advantage of the space group symmetry. The final step is in the form of a general application which is the same for all the space groups.

The specification of the origin is carried out in conformance with the seminvariant theory previously developed (Hauptman & Karle, 1953, 1959). It is the same for all space groups of a given type. In type $4P$, the origin is specified once the functional form for the structure factor has been chosen.

For the space groups of type $4P$, all the phases are seminvariants. This means that once the functional form of the structure factor has been chosen, the values of all phases are uniquely determined by the intensities alone. It is of interest to note, in the procedures to follow, how a single equation, (3.1.2) or (3.2.2), used in conjunction with relationships among the structure factors, characteristic of the particular space group and the chosen functional form of the structure factor, does, in fact, lead to unique values for all the phases.

4.1. Cubic system, I-centered

We are concerned here with space groups, $Im\bar{3}$, $Ia\bar{3}$, $Im\bar{3}m$ and $Ia\bar{3}d$. The special choices for \mathbf{h}_1 and \mathbf{h}_2 , in addition to $\mathbf{h}_1 = \mathbf{h}_2$, are shown in the first two rows of Tables 1 and 2. By means of the first choice in Table 1, $\mathbf{h}_1 = (h_1, k_1, h + \bar{k}_1)$ and $\mathbf{h}_2 = (\bar{h} + \bar{h}_1, h + \bar{k}_1, k_1)$, equation (3.1.2) or (3.2.2) yields the value of $\mathcal{E}'_{h_1, k_1, h + \bar{k}_1} \mathcal{E}'_{\bar{h}\bar{h}h}$ multiplied by the numerical coefficient given in the second column of Table 1. For example, for $P(Ia\bar{3})$, the relationship $\mathcal{E}'_{hkl} = (-1)^{h+k} \mathcal{E}'_{\bar{h} + \bar{k} + \bar{l}, l, k}$, following from the chosen functional form for the structure factor, gives rise to the entry $(-1)^{h_1+k_1}$ in column 2, Table 1. In this way the value of the phase $\varphi'_{\bar{h}\bar{h}h}$ is determined. Since h_1 and k_1 may be chosen arbitrarily, $\varphi'_{\bar{h}\bar{h}h}$ may possibly be determined in many ways. As always, the computations are performed for the larger values of $|\mathcal{E}'_{\mathbf{h}_1} \mathcal{E}'_{\mathbf{h}}|$. In the application of Tables 1 and 2, the entries in each of the columns are to be carried through cyclic permutations on the h, k and l , which would multiply the number of possible choices by three. For example, the entries of column 2, Table 1 may be permuted to give $\mathbf{h}_1 = k + \bar{l}_1, k_1, l_1, \mathbf{h}_2 = l_1, \bar{k} + \bar{k}_1, k + \bar{l}_1$ and $\mathbf{h} = k, \bar{k}, k$. They may be further permuted to give $\mathbf{h}_1 = h_1, l + \bar{h}_1, l_1, \mathbf{h}_2 = l + \bar{h}_1, h_1, \bar{l} + \bar{l}_1$ and $\mathbf{h} = l, l, \bar{l}$.

In the space groups of type $4P$, all the phases are seminvariants and thus their values may be directly obtained from the intensities. One of eight possible centers of symmetry, the origin for the unit cell, has already been specified by choosing one of the eight possible functional forms for the structure factor. We note that all the phases, φ'_{hkl} , obtained from Tables 1 and 2 are of a special type since there are restrictions on the h, k and l . By use of these phases, however, it is possible to calculate the values of additional phases with arbitrary subscripts. This is illus-

Table 3

Selected values of \mathbf{h}_1 and \mathbf{h}_2 to be inserted into (3·1·2) or (3·2·2) in order to obtain the product $\mathcal{E}'_{\mathbf{h}_1}\mathcal{E}'_{\mathbf{h}_2}\mathcal{E}'_{\mathbf{h}_1+\mathbf{h}_2}$ from which the value of an arbitrary phase φ'_{hkl} may be inferred. A knowledge of $\varphi'_{\mathbf{h}_1}$ and $\varphi'_{\mathbf{h}_2}$ is required and may be obtained by use of Table 1. Each column may undergo cyclic permutation

\mathbf{h}_1	$\bar{h} + \bar{k} + l,$	$h + k + l,$	$h + k + l$	h_1	$k + 2\bar{k}_1,$	l_1
\mathbf{h}_2	$2h + k + l,$	$\bar{h} + \bar{l},$	$\bar{h} + \bar{k}$	$h + \bar{h}_1,$	$2k_1,$	$l + \bar{l}_1$
$\mathbf{h} = \mathbf{h}_1 + \mathbf{h}_2$	$h,$	$k,$	l	$h,$	$k,$	l
Condition				$h_1 + l_1 \equiv k \pmod{2}$		

trated in Table 3. For column 2, Table 3, $\mathcal{E}'_{\mathbf{h}_1}$ is obtainable from column 2, Table 1 and $\mathcal{E}'_{\mathbf{h}_2}$ is obtainable from column 4, Table 1. Again, for column 3, Table 3, $\mathcal{E}'_{\mathbf{h}_1}$ is obtainable from column 5, Table 1 and $\mathcal{E}'_{\mathbf{h}_2}$ is obtainable from column 6, Table 1. Both columns 2 and 3 of Table 3 lead to the value of φ'_{hkl} for arbitrary h, k and l by use of (3·1·2) or (3·2·2). Since, in column 3, Table 3, k_1 is arbitrary and h_1 and l_1 are subject to only a mild restriction, the value of a phase may possibly be obtained in many ways. The entries in Table 3 may undergo cyclic permutation. Clearly, this table is merely illustrative and not exhaustive. All phases obtained from Tables 1, 2 and 3 may be used for continuing the phase determining procedure.

5. Concluding remarks

This paper should be read in conjunction with 1P (1959), in which the symbols are defined and general remarks are made which are applicable to all the space groups.

The phase determining procedures offer many ways to calculate the value of a particular phase. This feature, together with the fact that the calculation of the right sides of (3·1·2) and (3·2·2) should yield not only the sign of the left side, but also its magnitude, serves as a good internal consistency check as the phase determination proceeds.

Tables 1, 2 and 3 of this paper, and also the tables occurring in previous papers on this subject, have been prepared with care in order to avoid errors. The method of preparation has been illustrated and it is seen that it is a simple matter to check the entries. However, there are ninety-two centrosymmetric space groups, and thus many tables. We therefore recommend that the entries in the appropriate table be verified before an application of these methods is made to a particular space group for the first time.

The procedures discussed in the uniform program for phase determination for all the centrosymmetric space groups have confirmed the predictions of the seminvariant theory (Hauptman & Karle, 1953, 1959) regarding the type of phase whose value may be arbitrarily specified, as well as the nature of the linear combinations of one or more phases whose values may be computed from the intensities alone. Table 3 of this paper is a noteworthy illustration of this confirmation since it shows how the value of an arbitrary phase may be found without the necessity for the

previous specification of the value of any phase, in accordance with the seminvariant theory for type 4P.

6. Appendix

The correction terms for the formulas listed in § 3 are given here and in 1P (1959). As a general rule, for large N , they make a very small contribution. In any specific instance, the investigator can judge their importance for himself.

We define:

$$\begin{aligned}
 {}_{16}R_2, 0 = & -\frac{\sigma_8^{1/2}}{\sigma_4} \mathcal{E}'_{h+k, h+k, \bar{h}+\bar{k}} + \mathcal{E}'_{h+l, \bar{h}+\bar{l}, h+l} + \mathcal{E}'_{\bar{k}+\bar{l}, k+l, k+l} \\
 & - \frac{2\sigma_8^{1/2}}{\sigma_2\sigma_4^{1/2}} (p+q-4) \mathcal{E}'_{\mathbf{h}} \mathcal{E}'_{\mathbf{h}} \\
 & - \frac{\sigma_4}{4\sigma_2^2} ((p-2)(p-4) + (q-2)(q-4)) \mathcal{E}'_{\mathbf{h}^2} \\
 & + \frac{4\sigma_6}{\sigma_2\sigma_4} (p+q-4) \\
 & + \frac{\sigma_4}{16\sigma_2^2} ((p-2)(q-2) + 2(p-2)(p-4) \\
 & + 2(q-2)(q-4)) + \dots, \quad (6.1)
 \end{aligned}$$

$$\begin{aligned}
 {}_{17}R_2, 0 = & \varrho_1 - \frac{14\sigma_8^{1/2}}{\sigma_2\sigma_4^{1/2}} (p+q-4) \mathcal{E}'_{\mathbf{h}} \mathcal{E}'_{\mathbf{h}} \\
 & - \frac{7\sigma_4}{4\sigma_2^2} ((p-2)(p-4) + (q-2)(q-4)) \mathcal{E}'_{\mathbf{h}^2} \\
 & + \frac{49\sigma_6}{\sigma_2\sigma_4} (p+q-4) + \frac{7\sigma_4}{16\sigma_2^2} ((p-2)(q-2) \\
 & + 2(p-2)(p-4) + 2(q-2)(q-4)) + \dots, \quad (6.2)
 \end{aligned}$$

where,

$$\begin{aligned}
 \varrho_1 = & -\frac{\sigma_8^{1/2}}{\sigma_4} (3\mathcal{E}'_{h+k, h+k, \bar{h}+\bar{k}} + 3\mathcal{E}'_{h+l, \bar{h}+\bar{l}, h+l} \\
 & + 3\mathcal{E}'_{\bar{k}+\bar{l}, k+l, k+l} + \mathcal{E}'_{0, 0, h+k+2l} + \mathcal{E}'_{0, h+2k+l, 0} \\
 & + \mathcal{E}'_{2h+k+l, 0, 0} + \mathcal{E}'_{0, 0, \bar{h}+\bar{k}} + \mathcal{E}'_{0, h+\bar{l}, 0} + \mathcal{E}'_{\bar{k}+\bar{l}, 0, 0} \\
 & + \mathcal{E}'_{h+l, \bar{h}+\bar{l}, k+l} + \mathcal{E}'_{h+l, h+k, \bar{h}+\bar{k}} + \mathcal{E}'_{\bar{k}+\bar{l}, h+k, k+l}), \quad (6.3)
 \end{aligned}$$

$$\begin{aligned}
 {}_{16}R_3, 0 = & -\frac{\sigma_4^{1/2}}{8\sigma_2} ((r-2) \mathcal{E}'_{\mathbf{h}_1^2} + (p-2) \mathcal{E}'_{\mathbf{h}_2^2} \\
 & + (q-2) \mathcal{E}'_{\mathbf{h}_1+\mathbf{h}_2}) + \varrho_2 \quad (6.4)
 \end{aligned}$$

where,

$$\begin{aligned} \varrho_2 = & -\frac{\sigma_8^{1/2}}{\sigma_4} \mathcal{E}'_{\mathbf{h}_1} (\mathcal{E}'''_{h_1+h_2+k_2, h_2+k_1+k_2, \bar{h}_2+\bar{k}_2+l_1} \\ & + \mathcal{E}'''_{h_1+h_2+l_2, \bar{h}_2+k_1+\bar{l}_2, h_2+l_1+l_2} \\ & + \mathcal{E}'''_{h_1+\bar{k}_2+\bar{l}_2, k_1+k_2+l_2, k_2+l_1+l_2}) \\ & - \frac{\sigma_8^{1/2}}{\sigma_4} \mathcal{E}'_{\mathbf{h}_2} (\mathcal{E}'''_{h_1+h_2+k_1, h_1+k_1+k_2, \bar{h}_1+\bar{k}_1+l_2} \\ & + \mathcal{E}'''_{h_1+h_2+l_1, \bar{h}_1+k_2+\bar{l}_1, h_1+l_1+l_2} \\ & + \mathcal{E}'''_{h_2+\bar{k}_1+\bar{l}_1, k_1+k_2+l_1, k_1+l_1+l_2}) \\ & - \frac{\sigma_8^{1/2}}{\sigma_4} \mathcal{E}'_{\mathbf{h}_1+\mathbf{h}_2} (\mathcal{E}'''_{h_1+\bar{k}_2, \bar{h}_2+k_1, h_2+k_2+l_1+l_2} \\ & + \mathcal{E}'''_{h_1+\bar{l}_2, h_2+k_1+k_2+l_2, \bar{h}_2+l_1} \\ & + \mathcal{E}'''_{h_1+h_2+k_2+l_2, k_1+\bar{l}_2, \bar{k}_2+l_1}) + \dots, \end{aligned} \quad (6.5)$$

$$\begin{aligned} {}_{17}R_{3,0} = & -\frac{7\sigma_4^{1/2}}{8\sigma_2} ((r-2)\mathcal{E}'_{\mathbf{h}_1} + (p-2)\mathcal{E}'_{\mathbf{h}_2} \\ & + (q-2)\mathcal{E}'_{\mathbf{h}_1+\mathbf{h}_2}) + \varrho_3, \end{aligned} \quad (6.6)$$

where,

$$\begin{aligned} \varrho_3 = & -\frac{\sigma_8^{1/2}}{\sigma_4} \mathcal{E}'_{\mathbf{h}_1} (3\mathcal{E}'''_{h_1+h_2+k_2, h_2+k_1+k_2, \bar{h}_2+\bar{k}_2+l_1} \\ & + 3\mathcal{E}'''_{h_1+h_2+l_2, \bar{h}_2+k_1+\bar{l}_2, h_2+l_1+l_2} \\ & + 3\mathcal{E}'''_{h_1+\bar{k}_2+\bar{l}_2, k_1+k_2+l_2, k_2+l_1+l_2} \\ & + \mathcal{E}'''_{h_1+h_2+l_2, \bar{h}_2+k_1+\bar{l}_2, k_2+l_1+l_2} \\ & + \mathcal{E}'''_{h_1+\bar{k}_2+\bar{l}_2, k_1+k_2+l_2, h_2+l_1+l_2} + \mathcal{E}'''_{h_1+h_2+\bar{k}_2, \bar{h}_2+k_1+k_2, l_1} \\ & + \mathcal{E}'''_{h_1, k_1, h_2+k_2+l_1+2l_2} + \mathcal{E}'''_{h_1+h_2+l_2, h_2+k_1+k_2, \bar{h}_2+\bar{k}_2+l_1} \\ & + \mathcal{E}'''_{h_1+\bar{k}_2+\bar{l}_2, h_2+k_1+k_2, k_2+l_1+l_2} \\ & + \mathcal{E}'''_{h_1+h_2+k_2, \bar{h}_2+k_1+\bar{l}_2, h_2+l_1+l_2} \\ & + \mathcal{E}'''_{h_1+h_2+k_2, k_1+k_2+l_2, \bar{h}_2+\bar{k}_2+l_1} + \mathcal{E}'''_{h_1, k_1+k_2+\bar{l}_2, \bar{k}_2+l_1+l_2} \\ & + \mathcal{E}'''_{h_1+h_2+\bar{l}_2, k_1, \bar{h}_2+l_1+l_2} + \mathcal{E}'''_{h_1+2h_2+k_2+l_2, k_1, l_1} \\ & + \mathcal{E}'''_{h_1, h_2+k_1+2k_2+l_2, l_1}) \\ & - \frac{\sigma_8^{1/2}}{\sigma_4} \mathcal{E}'_{\mathbf{h}_2} (3\mathcal{E}'''_{h_1+h_2+k_1, h_1+k_1+k_2, \bar{h}_1+\bar{k}_1+l_2} \\ & + 3\mathcal{E}'''_{h_1+h_2+l_1, \bar{h}_1+k_2+\bar{l}_1, h_1+l_1+l_2} \\ & + 3\mathcal{E}'''_{h_2+\bar{k}_1+\bar{l}_1, k_1+k_2+l_1, k_1+l_1+l_2} \\ & + \mathcal{E}'''_{h_1+h_2+l_1, \bar{h}_1+k_2+\bar{l}_1, k_1+l_1+l_2} \\ & + \mathcal{E}'''_{h_2+\bar{k}_1+\bar{l}_1, k_1+k_2+l_1, h_1+l_1+l_2} + \mathcal{E}'''_{h_1+h_2+\bar{k}_1, \bar{h}_1+k_1+k_2, l_2} \\ & + \mathcal{E}'''_{h_2, k_2, h_1+k_1+2l_1+l_2} + \mathcal{E}'''_{h_1+h_2+l_1, h_1+k_1+k_2, \bar{h}_1+\bar{k}_1+l_2} \\ & + \mathcal{E}'''_{h_2+\bar{k}_1+\bar{l}_1, h_1+k_1+k_2, k_1+l_1+l_2} \\ & + \mathcal{E}'''_{h_1+h_2+k_1, \bar{h}_1+k_2+\bar{l}_1, h_1+l_1+l_2} \\ & + \mathcal{E}'''_{h_1+h_2+k_1, k_1+k_2+l_1, \bar{h}_1+\bar{k}_1+l_2} + \mathcal{E}'''_{h_2, k_1+k_2+\bar{l}_1, \bar{k}_1+l_1+l_2} \\ & + \mathcal{E}'''_{h_1+h_2+\bar{l}_1, k_2, \bar{h}_1+l_1+l_2} + \mathcal{E}'''_{2h_1+h_2+k_1+l_1, k_2, l_2} \\ & + \mathcal{E}'''_{h_2, h_1+2k_1+k_2+l_1, l_2}) \end{aligned}$$

$$\begin{aligned} & - \frac{\sigma_8^{1/2}}{\sigma_4} \mathcal{E}'_{\mathbf{h}_1+\mathbf{h}_2} (3\mathcal{E}'''_{h_1+\bar{k}_2, \bar{h}_2+k_1, h_2+k_2+l_1+l_2} \\ & + 3\mathcal{E}'''_{h_1+\bar{l}_2, h_2+k_1+k_2+l_2, \bar{h}_2+l_1} + 3\mathcal{E}'''_{h_1+h_2+k_2+l_2, k_1+\bar{l}_2, \bar{k}_2+l_1} \\ & + \mathcal{E}'''_{h_1+\bar{l}_2, h_2+k_1+k_2+l_2, \bar{k}_2+l_1} + \mathcal{E}'''_{h_1+h_2+k_2+l_2, k_1+\bar{l}_2, \bar{h}_2+l_1} \\ & + \mathcal{E}'''_{h_2+k_1, h_1+k_2, l_1+l_2} + \mathcal{E}'''_{h_1+h_2, k_1+k_2, \bar{h}_1+\bar{k}_1+\bar{l}_1+l_2} \\ & + \mathcal{E}'''_{h_1+\bar{l}_2, \bar{h}_2+k_1, h_2+k_2+l_1+l_2} + \mathcal{E}'''_{h_1+h_2+k_2+l_2, \bar{h}_2+k_1, \bar{k}_2+l_1} \\ & + \mathcal{E}'''_{h_1+\bar{k}_2, h_2+k_1+k_2+l_2, \bar{h}_2+l_1} + \mathcal{E}'''_{h_1+\bar{k}_2, k_1+\bar{l}_2, h_2+k_2+l_1+l_2} \\ & + \mathcal{E}'''_{h_1+h_2, k_2+l_1, k_1+l_2} + \mathcal{E}'''_{h_2+l_1, k_1+k_2, h_1+l_2} \\ & + \mathcal{E}'''_{h_1+h_2+\bar{k}_1+\bar{l}_1, k_1+k_2, l_1+l_2} \\ & + \mathcal{E}'''_{h_1+h_2, \bar{h}_1+\bar{k}_1+k_2+\bar{l}_1, l_1+l_2}) + \dots, \end{aligned} \quad (6.7)$$

Next we define (where $C_n(t)$ is replaced by C_n):

$$\begin{aligned} {}_{16}R'_{2,0} = & -\frac{\sigma_8^{1/2}}{\sigma_4} (\mathcal{E}'''_{h+k, h+k, \bar{h}+\bar{k}} + \mathcal{E}'''_{h+l, \bar{h}+\bar{l}, h+l} \\ & + \mathcal{E}'''_{\bar{k}+\bar{l}, k+l, k+l}) + \frac{4\sigma_8^{1/2}}{C_1\sigma_2\sigma_4^{1/2}} (2C_1 - C_2)\mathcal{E}'_{\mathbf{h}}\mathcal{E}'''_{\mathbf{h}} \\ & - \frac{\sigma_4}{2C_1\sigma_2^2} (8C_1 - 6C_2 + C_3)\mathcal{E}'_{\mathbf{h}}{}^2 - \frac{4\sigma_6}{C_1\sigma_2\sigma_4} (2C_1 - C_2) \\ & + \frac{\sigma_4}{16C_1^2\sigma_2^2} ((2C_1 - C_2)^2 + 4C_1(8C_1 - 6C_2 + C_3)) + \dots, \end{aligned} \quad (6.8)$$

$$\begin{aligned} {}_{17}R'_{2,0} = & \varrho_1 + \frac{28\sigma_8^{1/2}}{C_1\sigma_2\sigma_4^{1/2}} (2C_1 - C_2)\mathcal{E}'_{\mathbf{h}}\mathcal{E}'''_{\mathbf{h}} \\ & - \frac{7\sigma_4}{2C_1\sigma_2^2} (8C_1 - 6C_2 + C_3)\mathcal{E}'_{\mathbf{h}}{}^2 \\ & - \frac{98\sigma_8}{C_1\sigma_2\sigma_4} (2C_1 - C_2) + \frac{7\sigma_8}{16C_1^2\sigma_2^2} \\ & \times ((2C_1 - C_2)^2 + 4C_1(8C_1 - 6C_2 + C_3)) + \dots, \end{aligned} \quad (6.9)$$

$$\begin{aligned} {}_{16}R'_{3,0} = & \frac{\sigma_4^{1/2}}{8C_1\sigma_2} (2C_1 - C_2) (\mathcal{E}'_{\mathbf{h}_1} + \mathcal{E}'_{\mathbf{h}_2} + \mathcal{E}'_{\mathbf{h}_1+\mathbf{h}_2}) + \varrho_2, \end{aligned} \quad (6.10)$$

and

$${}_{17}R'_{3,0} = \frac{7\sigma_4^{1/2}}{8C_1\sigma_2} (2C_1 - C_2) (\mathcal{E}'_{\mathbf{h}_1} + \mathcal{E}'_{\mathbf{h}_2} + \mathcal{E}'_{\mathbf{h}_1+\mathbf{h}_2}) + \varrho_3. \quad (6.11)$$

In order to summarize the relations among the correction terms for the various space groups in type $4P$, it is convenient to identify

$$R \equiv R^{(0)}, \quad (6.12)$$

$$R' \equiv R^{(1)}. \quad (6.13)$$

Thus, for space groups $Im\bar{3}$ and $Ia\bar{3}$,

$$R_{i,0}^{(j)} = {}_{16}R_{i,0}^{(j)} + {}_{16}R_{i,0}^{(j)}; \quad j=0, 1; \quad i=2, 3. \quad (6.14)$$

For space groups $Im3m$ and $Ia3d$,

$$R_{i,0}^{(j)} = {}_1R_{i,0}^{(j)} + {}_{17}R_{i,0}^{(j)}; \quad j=0, 1; \quad i=2, 3. \quad (6.15)$$

Note that, ${}_1R_{2,0}$, ${}_1R_{3,0}$, ${}_1R'_{2,0}$ and ${}_1R'_{3,0}$ are defined in 1P (1959).

The remainder terms in the basic formulas are especially simple for the special case $p=q=r=2$. For this case, the formulas reduce to those obtainable by the algebraic methods proposed by us (1957).

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Désordre Statistique dans la Structure du Bromo₉-Méthyl₁₀-Anthracène

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9-Bromo-10-méthylantracène is isotypic with 9-cyanoanthracène. The molecules are statistically distributed so that bromine substitutes for methyl and *vice versa*. Short-range order is detectable.

1. Maille. Groupe spatial

Le Bromo₉-méthyl₁₀-anthracène se présente sous forme d'un enchevêtrement de fines aiguilles jaunes, allongées suivant la direction [001]; en cristallisant dans un mélange (1/3 alcool + 2/3 benzène), on a obtenu des aiguilles de 0,3 mm. de diamètre. Les clichés de diffraction (rétigrammes) ont été effectués avec la radiation Cu $K\alpha$.

La maille orthorhombique est très voisine de celle du cyano₉-anthracène (Rabaud & Clastre, 1959).

2. Structure

Le Tableau 1 montre que les deux structures sont isomorphes. On constate en effet que les substituants brome et méthyl de notre composé occupent dans la maille des positions très voisines de celles du groupelement (CN)₉ et de l'atome H₁₀ du cyananthracène.

L'examen de la fonction de Patterson montre que le substituant Q possède une masse électronique environ 3 fois supérieure à celle que l'on attendrait d'un CH₃, alors que le substituant P possède une masse électronique égale aux 2/3 environ de celle d'un

Tableau 1

	Br ₉ -Mé ₁₀ - anthracène	Cyano ₉ - anthracène
a	17,6 Å	17,1 Å
b	16,2	15,1
c	3,98	3,93
Z (nombre mol./maille)	4	4
Groupe de symétrie	$P2_12_1$	$P2_12_1$
Point de fusion	171 °C.	173 °C.

Tableau 2

Atome P	Br ₉ -Mé ₁₀ - anthracène	Cyano ₉ -anthracène		
	(Br)	C	N	Moyenne
x/a	0,578	0,552	0,584	0,568
y/b	0,214	0,240	0,178	0,209
z/c	0,25	0,285	0,190	0,237
Atome Q	(CH ₃)	Atome H (positions présumées)		
x/a	0,361	0,398		
y/b	0,525	0,521		
z/c	0,72	0,687		

atome de brome. Cependant la pureté du produit ne peut être mise en doute.

Ce phénomène s'explique par un échange du brome et du méthyl, qui occupent statistiquement les positions appelées P et Q .

Nous avons voulu préciser cet échange de substituants en effectuant une série de fonctions-différence sur la projection (001). Cette projection fait intervenir 360 taches pqo et les molécules, vues presque à plat y sont distinctes les unes des autres.

(a) Positions des atomes lourds

Nous avons pu montrer que, d'une part, les sites P et Q sont simples — l'atome Br vient exactement en position du méthyl et réciproquement — que, d'autre part, les masses électroniques (statistiques) placées sur ces sites équivalent à:

$$P = 0,60(\text{Br}) + 0,40(\text{CH}_3) = 23,4 \text{ électrons}$$

$$Q = 0,60(\text{CH}_3) + 0,40(\text{Br}) = 17,6 \text{ électrons}$$

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