Apart from the value 2·88 for s_{11} obtained by Voigt (1910), and the value 2·69 obtained by Doraiswami (1947), values have been given by Tutton (1922) (3·47) and by Birch (1950) (2·64). The present value of s_{11} therefore falls within the range observed by others.

The accuracy of the determination of χ_{44} is about ±0·04 if reasonable variations are allowed for possible error in determination of the density distribution on the photograph and in the determination of the position on the photograph corresponding to particular rekhas. The accuracy of the determination of χ_{12} is lower than that of χ_{44}. We may obtain an indication of the range of values of c_{12} consistent with the present observations from the different values of χ_{12} obtained from the photographs. The form of the contours in Fig. 1(b) is affected by the value of χ_{12} but not so markedly as to permit a precise determination of c_{12}. The roughly estimated range of possible values of c_{12} is ±2×10¹¹, the mean value being 3×10¹¹ dyne cm.⁻².

References

BHAGAVANTAM S. & BHIMASENACHAR J. (1944). *Proc. Indian Acad. Sci.* **20**, 298.

BHAGAVANTAM, S. & BHIMASENACHAR, J. (1946). *Proc. Roy. Soc.* A, **187**, 381.

BHIMASENACHAR, J. (1950). *Proc. Nat. Inst. Sci. India*, **16**, 241.

BIRCH, F. (1950). *Amer. Min.* **35**, 644.

BRIDGMAN, P. W. (1949). *Proc. Amer. Acad. Arts Sci.* **77**, 189.

DORAISWAMI, M. S. (1947). *Proc. Indian Acad. Sci.* A, **25**, 413.

HOERNI, J. & WOOSTER, W. A. (1952). *Acta Cryst.* **5**, 626.

RAMACHANDRAN, G. N. & WOOSTER, W. A. (1951). *Acta Cryst.* **4**, 335.

SCHMID, E. & BOAS, W. (1935). *Kristallplastizität.* Berlin: Springer.

SMITH, F. G. (1942). *Amer. Min.* **27**, 1.

TUTTON, A. E. H. (1922). *Crystallography and Practical Crystal Measurement,* vol. 2, p. 1348. London: Macmillan.

VOIGT, W. (1910). *Lehrbuch der Kristallphysik.* Leipzig: Teubner.

WOOSTER, W. A. (1955). *J. Sci. Instrum.* **32**, 457.

A Re-determination of the Structure of Triphenylene

By P. R. PINNOCK, C. A. TAYLOR AND H. LIPSON

Physics Department, College of Technology, Manchester 1, England

The structure of triphenylene derived by Klug is unconvincing because there are some large discrepancies between calculated and observed structure amplitudes, although the agreement residuals (0·20 for hk0 and 0·32 for 0kl reflexions) appear to be satisfactory. The present paper describes an independent attempt to derive the structure from Klug's data: the molecular orientation is found by means of optical-transform principles (and turns out to be the same as that found by Klug); the molecular position is found by means of Taylor's method, which is based upon selected zero or weak reflexions. A result different from that of Klug is obtained; it gives better agreement with the observed data and gives no anomalous intermolecular distances.

1. Reasons for re-determining the structure

The crystal structure of triphenylene described by Klug (1950) has some properties that cast doubt upon its validity. First, although reasonably low agreement residuals are reported (0·20 for hk0 and 0·32 for 0kl reflexions), there are some individual discrepancies that are too large to be accepted. The most prominent of these are shown in Table 1.

Secondly, some of the distances (e.g. 2·58 Å) between atoms in neighbouring molecules are too small to correspond to ordinary van der Waals forces (Robertson, 1953; Jdanov & Zvonkova, 1954; Vand & Pepinsky, 1954).

Table 1. *Some discrepancies in Klug's results*

hkl	310	330	350	430	440	021	031	074
$|F_o|$	61	54	19	< 5	38	22	< 4	10
F_c	20	−28	−10	−14	15	−6	20	26

It was therefore decided to see whether Klug's data could be satisfied by another structure, which would give at least as good general agreement as Klug's structure and would give no discrepancies comparable with those listed in Table 1. It was hoped that, if such a structure could be found, it would settle the problem of the anomalous distances.

2. Crystallographic data

The data given by Klug are as follows:

Space group: No. 19, $P2_12_12_1$.
$a = 13\cdot20$, $b = 16\cdot84$, $c = 5\cdot28$ Å.
Number of molecules in unit cell: 4.

In this space group the molecules are necessarily in general positions.

3. Determination of molecular positions

Hanson, Lipson & Taylor (1953) have shown, by optical-transform methods, that the $hk0$ weighted reciprocal lattice drawn from Klug's data supports his choice of molecular orientation made from consideration of the intensities of the $h00$ and $0k0$ reflexions. This choice was based upon the deduction of the orientation of the molecular plane by Banerjee & Guha (1937), who measured the magnetic anisotropy; the results of Hanson et al. show that the X-ray data are sufficient in themselves to fix the molecular orientation.

Fig. 1 illustrates the basis of the method. It shows a representation of the optical transform of the projection of a single molecule, in the orientation derived, superimposed upon the weighted reciprocal lattice; the strong reflexions are satisfied either by the peaks of the transform itself or by the mirror image produced by the symmetry elements of the plane group, pgg, to which this projection belongs.

It will be observed that not all the reciprocal-lattice points that fall on transform peaks correspond to large
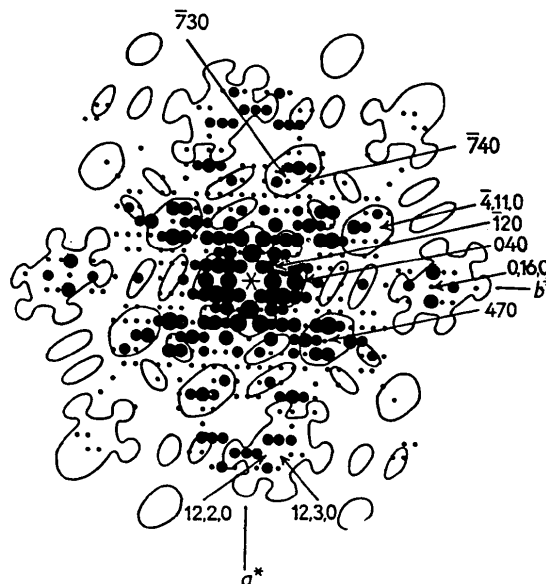

Fig. 1. The $hk0$ weighted reciprocal-lattice section superimposed upon a representation of the optical transform of a single correctly orientated molecule. The arrows indicate the reflexions used for the application of Taylor's method (two of them—$\bar{1}20$ and 040—are strong reflexions which do not give results as reliable as those given by the weaker reflexions).

X-ray intensities; some of the intensities are weak because of the interference of the transforms of the four molecules in the unit cell. These are the reflexions that are used in the method described by Taylor (1954)
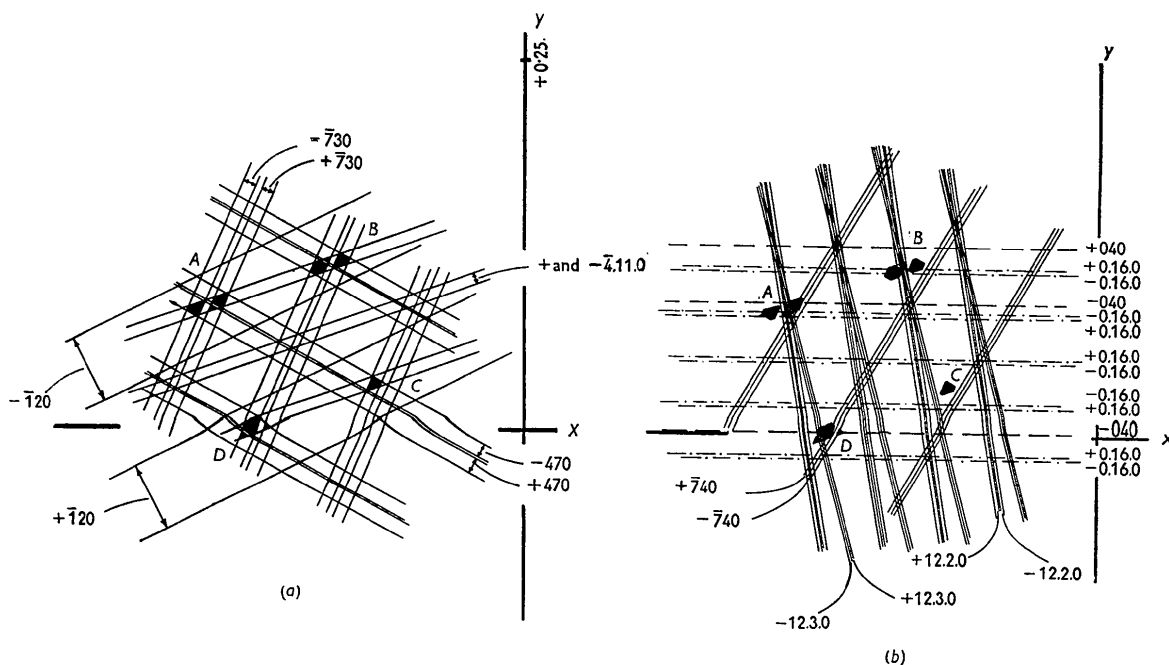

Fig. 2. The application of Taylor's method to the (001) projection. (a) The derivation of four solutions indicated by the blackened regions A, B, C and D. (b) The use of higher orders to eliminate all but the region A.

for finding molecular positions, and they must satisfy the following conditions:

(i) Each observed structure amplitude must be small.
(ii) Each reciprocal-lattice point must lie on a strong part of the transform in one quadrant and on a weak part in the adjacent quadrant.
(iii) The points should be as far as possible evenly distributed over the reciprocal lattice.

The reflexions chosen are indicated on Fig. 1 and the result of applying the method is shown in Fig. 2. There is a unique solution, $x = 0.208 \pm 0.003$, $y = 0.079 \pm 0.003$ with respect to a centre of symmetry of the projection, a result quite different from the values given by Klug, $x = 0.175$, $y = 0.140$. Refinement of the projection was carried out by ordinary Fourier methods, aided by the optical method of determining the signs of the structure factors described by Pinnock & Taylor (1955).

The structure factors were calculated with the atomic scattering factors published in the *International Tables*, the temperature factor being then derived empirically. In deriving the temperature factor it was found that the scale of the published structure amplitudes was too high; to obtain the best fit of calculated and observed structure amplitudes it was found necessary to reduce the scale of the latter by a factor of 0.57.

Taylor's method was used also for the (100) projection and the twelve reflexions used gave an unambiguous result $y = 0.168 \pm 0.003$, $z = 0.050 \pm 0.005$. The value of y is in excellent agreement with that determined from the $hk0$ intensities; because of the changes in origin usually resorted to in dealing with projections of the space group $P2_12_12_1$, the sum of the values should be 0.250. The parameters were refined by the use of structure-factor graphs for those reflexions most greatly in error, and then by ordinary Fourier methods; but because of the considerable overlapping in this projection the movements of the atoms were rather uncertain, and the agreement residual did not reach as low a value as that for the $hk0$ reflexions. Klug (1950) states that the $0kl$ reflexions were probably measured less accurately than the $hk0$ reflexions.

4. Hydrogen atoms

As reported by Pinnock & Lipson (1954), the observed $hk0$ structure amplitudes are good enough to allow the detection of the hydrogen atoms. The $0kl$ data do not appear to be so good, and the z parameters of the hydrogen atoms cannot be found. It is therefore possible to report only that the hydrogen atoms lie approximately in the plane of the molecule, at distances of about 1·1 Å from the carbon atoms.

5. Extinction

When the refinement of the (001) projection had proceeded as far as seemed practicable, it was noted

that the strongest intensities all had consistently high calculated values (Pinnock & Lipson, 1954). It was presumed that this discrepancy was caused by extinction and an empirical correction was applied in the following way.

Secondary extinction can be regarded as equivalent to an increase, for each individual reflexion, of the linear absorption coefficient μ, the increase being proportional to the intensity of the reflexion (Darwin, 1922). Thus I, the intensity that would be observed in the absence of extinction, is reduced to the observed value I_o by the ratio $\mu/(\mu+gI)$, where g is a constant. If we take I to be equal to I_c, the value obtained by calculation, then

$$\frac{I_c}{I_o} = 1 + \frac{g}{\mu} I_c.$$

Thus, if I_c/I_o is plotted against I_c a straight line should result.

This relationship was tested by taking $I(hkl) = LpF^2(hkl)$, where L is the Lorentz factor and p is the polarization factor. The result is shown in Fig. 3. It
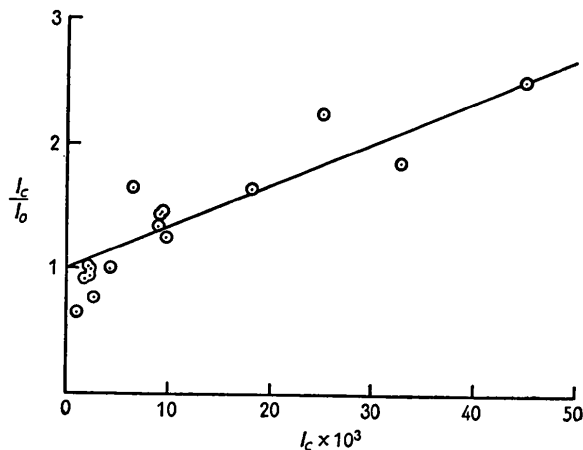

Fig. 3. Correction for secondary extinction.

supports the theory fairly well and gives a value of g/μ of 0.034; if this is accepted, the strongest reflexion 200 is so strongly affected by extinction that the observed intensity is less than half of the true value.

In Tables 2 and 3 the observed and calculated structure amplitudes for the $hk0$ and $0kl$ reflexions are compared; the values indicated by an asterisk are those corrected for extinction. The agreement residual for the $hk0$ zone is reduced from 0.21 to 0.17 by the correction. The residual for the $0kl$ zone is 0.35 and is not greatly affected by the extinction correction. (The residuals are calculated only for those reflexions for which Klug gives values or an upper limit; for the latter the observed value is taken as half the upper limit.)

The final Fourier syntheses were calculated with Klug's values re-scaled and corrected for extinction; the projections on the (001) and (100) planes, obtained by X-RAC (Pepinsky, 1947), are shown in Fig. 4.

Table 2. *Observed and calculated values of the* $(hk0)$ *structure factors*

(Origin on 2_1 axis parallel to c)

$hk0$	$|F_o|$	F_c	$hk0$	$|F_o|$	F_c	$hk0$	$|F_o|$	F_c	$hk0$	$|F_o|$	F_c
*200	73	$\bar{73}$	230	15	18	520	5	$\bar{3}$	820	<2	2
400	9	7	240	10	$\bar{7}$	530	5	$\bar{9}$	830	19	$\bar{18}$
600	11	12	250	3	$\bar{3}$	540	16	13	840	28	$\bar{24}$
800	10	6	260	9	$\bar{2}$	550	13	10	850	18	$\bar{15}$
10,0,0	<3	$\bar{4}$	270	9	$\bar{5}$	560	30	28	860	9	$\bar{6}$
12,0,0	22	$\bar{17}$	280	9	$\bar{7}$	570	16	16	8,13,0	6	6
			290	<2	$\bar{4}$	580	<2	2			
*020	43	48	2,10,0	10	$\bar{8}$	590	<2	$\bar{3}$	910	<3	$\bar{6}$
*040	40	$\bar{42}$	2,11,0	7	3	5,10,0	7	0	920	<3	$\bar{4}$
060	14	$\bar{15}$				5,11,0	17	$\bar{15}$	930	11	$\bar{9}$
080	9	$\bar{13}$	*310	40	42	5,12,0	10	8	940	9	9
0,10,0	14	13	320	19	$\bar{18}$				950	<3	0
0,12,0	7	$\bar{6}$	*330	33	$\bar{31}$	610	6	$\bar{2}$	960	9	$\bar{8}$
0,14,0	17	21	*340	27	26	620	12	8	9,10,0	8	$\bar{5}$
0,16,0	7	$\bar{4}$	350	11	$\bar{10}$	630	9	$\bar{5}$			
0,18,0	15	$\bar{17}$	*360	27	$\bar{21}$	640	8	6	10,4,0	7	9
0,20,0	7	7	*370	34	$\bar{32}$	650	10	$\bar{7}$			
			380	22	$\bar{20}$	660	<2	$\bar{2}$	11,1,0	<3	4
*110	28	27	390	11	6	670	10	$\bar{8}$	11,2,0	14	17
*120	64	60	3,10,0	12	$\bar{10}$	680	8	$\bar{6}$	11,3,0	21	21
*130	36	$\bar{37}$	3,11,0	10	11	690	<2	$\bar{3}$	11,4,0	17	19
*140	31	$\bar{36}$	3,12,0	7	$\bar{3}$	6,10,0	8	$\bar{7}$	11,14,0	5	3
*150	23	23				6,11,0	7	4	11,15,0	6	$\bar{5}$
160	16	10	410	<2	$\bar{3}$						
170	9	$\bar{6}$	*420	25	$\bar{23}$	710	6	$\bar{4}$	12,1,0	14	$\bar{19}$
180	5	$\bar{2}$	430	<2	$\bar{3}$	720	18	$\bar{15}$	12,2,0	<3	$\bar{2}$
1,13,0	7	3	440	22	19	730	7	4	12,3,0	<3	0
1,14,0	8	3	*450	34	29	740	<2	$\bar{3}$	12,4,0	10	5
1,15,0	<2	7	460	17	18	750	<2	$\bar{2}$	12,5,0	8	3
1,16,0	31	30	470	8	8	760	5	4	12,13,0	10	10
1,17,0	10	$\bar{8}$	480	<2	0	770	<2	$\bar{3}$	12,14,0	10	$\bar{9}$
1,18,0	7	10	490	28	$\bar{29}$	780	9	$\bar{10}$			
			4,10,0	22	19	7,12,0	11	10	13,1,0	10	$\bar{10}$
									13,2,0	15	$\bar{18}$
210	13	14	—510	18	11	810	8	$\bar{5}$	13,3,0	10	$\bar{11}$
*220	51	$\bar{53}$									

* Values corrected for extinction.

Table 3. *Observed and calculated values of the* $(0kl)$ *structure factors*

(Origin on 2_1 axis parallel to a)

$0kl$	$|F_o|$	F_c	$0kl$	$|F_o|$	F_c	$0kl$	$|F_o|$	F_c	$0kl$	$|F_o|$	F_c
*020	43	$\bar{48}$	061	8	$\bar{1}$	042	19	20	014	3	$\bar{2}$
*040	40	$\bar{42}$	071	<2	4	052	10	6	024	<2	$\bar{4}$
060	14	15	081	7	5	062	17	$\bar{19}$	034	2	$\bar{4}$
080	9	$\bar{13}$	091	9	$\bar{9}$	072	13	11	044	2	$\bar{5}$
0,10,0	14	$\bar{13}$	0,10,1	<2	$\bar{4}$	082	3	3	055	9	$\bar{7}$
0,12,0	7	$\bar{6}$	0,11,1	6	12	092	7	9	064	10	$\bar{6}$
0,14,0	17	$\bar{21}$	0,12,1	4	1	0,10,2	<2	$\bar{4}$	074	6	3
0,16,0	7	$\bar{4}$	0,13,1	5	$\bar{8}$	0,11,2	11	$\bar{15}$	084	6	10
0,18,0	15	17	0,14,1	3	$\bar{3}$	0,12,2	16	$\bar{17}$	094	4	9
0,20,0	7	7	0,15,1	9	7				0,10,4	10	14
			0,16,1	6	5	013	<2	6			
002	9	10	0,17,1	<2	$\bar{1}$	023	2	$\bar{1}$	015	3	2
004	3	$\bar{9}$	0,18,1	3	$\bar{3}$	033	6	$\bar{2}$	025	2	3
006	7	3	0,19,1	2	3	043	<2	0	075	3	4
			0,20,1	4	2	053	11	13			
011	<2	$\bar{1}$				063	3	$\bar{2}$	016	7	$\bar{5}$
021	13	24	012	7	$\bar{7}$	073	6	$\bar{14}$	026	6	$\bar{12}$
031	<2	$\bar{1}$	022	9	$\bar{12}$	083	<2	4	036	5	$\bar{4}$
041	14	$\bar{20}$	032	11	$\bar{24}$	0,15,3	4	6			
051	6	$\bar{5}$									

* Values corrected for extinction.

6. Results and description of the structure

The parameters of the atoms giving the results shown in Tables 2 and 3 are shown in Table 4. Although there are no large discrepancies such as those shown in Table 1, some of the weaker reflexions do not agree well. The agreement residuals—0·17 and 0·35—do not
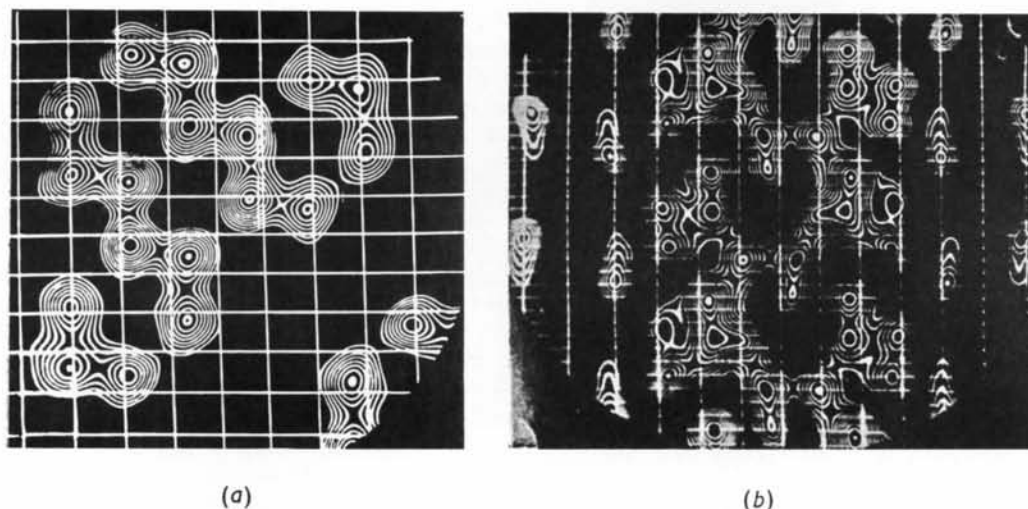
(a)   (b)

Fig. 4. (a) The (001) Fourier projection obtained by X-RAC. (b) The (100) Fourier projection obtained by X-RAC.

Table 4. *Atomic parameters*

Atom	x/a	y/b	z/c
1	0·441	0·700	0·60
2	0·523	0·699	0·41
3	0·531	0·641	0·22
4	0·614	0·639	0·04
5	0·692	0·701	0·08
6	0·769	0·704	−0·09
7	0·779	0·646	−0·30
8	0·711	0·583	−0·31
9	0·629	0·580	−0·15
10	0·556	0·515	−0·13
11	0·569	0·456	−0·34
12	0·493	0·400	−0·42
13	0·412	0·401	−0·19
14	0·400	0·451	−0·01
15	0·473	0·516	−0·01
16	0·459	0·578	0·19
17	0·379	0·580	0·35
18	0·367	0·636	0·54

include many of the unobserved reflexions, which are not included in Klug's tables, and thus the agreement cannot be considered particularly good. The z parameters probably contain the greatest errors. Attempts to reduce the $0kl$ residual below 0·35 were unsuccessful, a fact probably related to Klug's statement that the $0kl$ intensities suffer seriously from absorption errors.

Despite the lack of good general agreement, the packing of the molecules seems reasonable; there are several intermolecular distances below 4·0 Å, the smallest being 3·67 Å. This crystal therefore provides no evidence of a new type of intermolecular force, as discussed by Klug.

The poorness of agreement is reflected more in the improbable values of some of the intramolecular distances; these vary from 1·3 Å to 1·6 Å, and some of the atoms lie as much as 0·3 Å from the mean plane of the molecule. Fig. 5 shows an accurate diagram of the projection of the molecule on the (001) plane, and the departure from regularity is obvious. The extreme

discrepancies occur in those distances, such as LM and MN, that have large components perpendicular to the (001) plane; distances such as RA and HG, which are almost parallel to the (001) plane, are all included in the range 1·43±0·05 Å. Nevertheless, errors in the x and y parameters are probably also appreciable; in Fig. 5 the projected distance MN is much less than corresponding distances, such as QR and GF, in other parts of the molecule. As a test of the significance of this observation, the structure factors were re-calculated with atom M moved to a position more in conformity with the other atoms; the agreement residual was increased by 0·01.

For these reasons, it is considered inadvisable to publish complete structural details. The present work must be considered as a preliminary investigation, to be completed by those who are more able to assess whether the importance of the precise results would justify a complete re-determination of the experimental data.
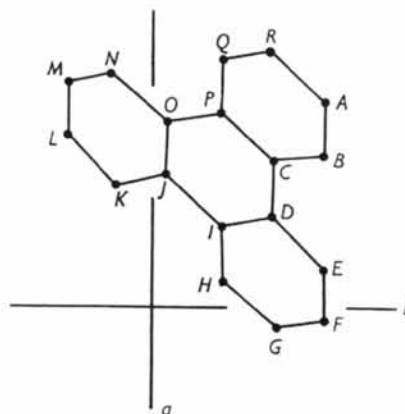

Fig. 5. Representation of projection of single molecule on (001).

7. Dependability of the result

In view of these conclusions, it may be asked whether the present work does provide a firm basis for a future investigation; sometimes the attainment of a residual no lower than 0·3 indicates that a structure is incorrect, but that it has some relationship to the correct structure (Dunitz & Robertson, 1947). For three reasons, it is unlikely that the present work suffers from this deficiency, if it is accepted that the molecular orientation has been correctly determined: (a) The application of Taylor's method to two independent sets of data yields unambiguous answers, with consistent y parameters. Since the method is based upon weak reflexions only, the results are not dependent upon accuracy of measurement. (b) The agreement residual for the $hk0$ reflexions is satisfactorily low. (c) The intermolecular distances are in conformity with those in other similar structures. Vand & Pepinsky (1954) have shown that, with the given orientation, there is only one arrangement of molecules with reasonable intermolecular distances, and this is the one presented in the present paper.

8. General discussion

The low values of the agreement residual—0·20 and 0·32—quoted by Klug, for what is now known to be an incorrect structure, require some comment; if such low values were true, it might be thought that the work would throw some doubt on many crystal-structure determinations. It cannot, however, be too strongly emphasized that the agreement residuals alone should not be used as the test of a structure (Lipson & Cochran, 1953); individual reflexions are more important, and in spite of the low value of the $hk0$ residual the discrepancies shown in Table 1 are sufficient to cast doubt upon the result.

Nevertheless, it was thought worth while to check Klug's results, and the values of $F(hk0)$ and $F(0kl)$ were re-calculated with the parameters quoted in his paper. Considerable differences were found, and the agreement residuals turned out to be much higher than those quoted—0·50 and 0·42. It is difficult to see how these errors have arisen. The results illustrate the importance of checking the calculation of the structure factors corresponding to the published parameters in any crystal-structure determination.

The re-calculated values of the residuals are still considerably less than the value of 0·83 given by Wilson (1950) for a randomly incorrect centrosymmetrical structure. This is so because Klug had correctly derived the molecular orientation; the transform peaks therefore lay in the correct position to account for the strong reflexions and so some measure of agreement must be obtained. From the point of view of the Patterson synthesis, the intramolecular vectors are correct, and only the intermolecular vectors are wrong.

This difficulty is always likely to arise when a symmetrical molecule like triphenylene is concerned. In-correct placing of a correctly oriented molecule is evidenced by a fairly low agreement residual with some individual large discrepancies. If, therefore, such circumstances arise, it is probable that the orientation of the molecule is correct and that a new position can be found that gives acceptable agreement for all reflexions.

It may be thought that the Fourier synthesis published by Klug is surprisingly good for an incorrect structure. Fourier synthesis, however, is not a good test of a proposed structure; it always tends to support the hypothesis upon which it is based. Since Klug's deductions from the Fourier transform were correct, the synthesis gave a recognizable representation of the molecules in the positions in which they were assumed to lie. The results should, however, be much better than this; the peaks should be reasonably symmetrical in shape and their heights should be nearly equal, whereas in Klug's synthesis the heights vary almost by a factor of two.

These considerations emphasize the extreme care that must be taken before a structure is put forward as correct.

References

BANERJEE, S. & GUHA, A. C. (1937). *Z. Kristallogr.* **96**, 107.

DARWIN, C. G. (1922). *Phil. Mag.* **43**, 800.

DUNITZ, J. D. & ROBERTSON, J. M. (1947). *J. Chem. Soc.* p. 1145.

HANSON, A. W., LIPSON, H. & TAYLOR, C. A. (1953). *Proc. Roy. Soc.* A, **218**, 371.

JDANOV, G. S. & ZVONKOVA, Z. V. (1954). *Travaux de l'Institut de Cristallographie*, **10**, 79.

KLUG, A. (1950). *Acta Cryst.* **3**, 165.

LIPSON, H. & COCHRAN, W. (1953). *The Determination of Crystal Structures*, p. 145. London: Bell.

PEPINSKY, R. (1947). *J. Appl. Phys.* **18**, 601.

PINNOCK, P. R. & LIPSON, H. (1954). *Acta Cryst.* **7**, 594.

PINNOCK, P. R. & TAYLOR, C. A. (1955). *Acta Cryst.* **8**, 687.

ROBERTSON, J. M. (1953). *Organic Crystals and Molecules*, p. 202. Ithaca: Cornell University Press.

TAYLOR, C. A. (1954). *Acta Cryst.* **7**, 757.

VAND, V. & PEPINSKY, R. (1954). *Acta Cryst.* **7**, 595.

WILSON, A. J. C. (1950). *Acta Cryst.* **3**, 397.