# THE STRUCTURE OF ANTHRAQUINONE
# ( A QUANTITATIVE X-RAY INVESTIGATION )

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Plates XIVA and XIVB

ABSTRACT. Complete structural analysis of anthraquinone crystal has been carried out. It has been proved from X-ray, goniometric and optical studies that anthraquinone does not belong to the orthorhombic class of crystals as was concluded by the earlier workers but it really belongs to the monoclinic class, the correct space group being $C_{2h}^5 P_{2_1}/a$ with two molecules per unit cell. On the basis of the revised space group, it has also been possible to account for a number of observed discrepancies which could not be explained on the basis of the orthorhombic hypothesis

Quantitative X-ray investigation has led to a complete determination of the structure of anthraquinone by means of three two-dimensional Fourier syntheses Precise orientation of the molecules in the crystal and the co-ordinates of the atoms are given. The results obtained show that anthraquinone molecule is planar and centro symmetrical The two outer benzene rings are almost regular hexagons, the distance between the carbon atoms being 1.38-1.40 Å ($\pm$ 01 A). The inner benzene ring shows distortion somewhat similar to that in the benzoquinone molecule, the "single" bond C-C distance being 1.50 Å, which is exactly the same as found in benzoquinone. The carbon-oxygen distance in anthraquinone works out as 1 15 Å, which is also almost the same as determined in benzoquinone.

The dominant feature found in the structure of anthraquinone crystal is the grouping of molecules in a zig-zag way in space with the molecular planes in the alternative layers being inclined to one another at an angle of 54°. The minimum intermolecular approach distances are of the order of 3.5 Å, similar to the distances found in other aromatic hydrocarbons.

## INTRODUCTION

The structure analysis of anthraquinone is highly interesting, particularly from the point of view of chemists on account of the importance of this compound in organic chemistry. It is interesting whether the valency bonds in the central benzene ring of anthraquinone are similar to those in benzoquinone or are they distorted in a different fashion under influence of the two outer rings. It was also to be seen whether the two outer rings of anthraquinone are distorted under influence of the substitution of oxygen atoms to the central ring or do the outer rings remain regular hexagons just as in the case of anthracene.

Previous attempts to determine the structure of anthraquinone crystal were made by Caspari (1932), Hertel and Romer (1931), Banerjee and Guha (1934-35), but with no conclusive results. All these workers had assumed

the anthraquinone crystal to be orthorhombic after Groth's (1906-19) data. Guha (1938) had also tried to determine the structure of anthraquinone by the 'trial and error' method but without success.

## DETERMINATION OF SPACE-GROUP OF ANTHRAQUINONE

On the basis of the space-group $D_{2h}^{13}Pmmn$ as tentatively assumed by Banerjee and Guha (1934-5) for anthraquinone, a determination of structure as projected on (001) plane was carried out by the two-dimensional Fourier summation method (Bragg, 1929) after necessary intensity measurements. After a few trials, satisfactory agreement between the measured and calculated values of structure factors was attained and the Fourier summation also gave a clear electron map. The following peculiar points were, however, noticed during this analysis and were at that time considered to be spurious as they could not be accounted for on the basis of the accepted orthorhombic space group :—

(a) Too many symmetries were obtained in the unit cell which were more than that required by the space-group. These appeared from the observed conditions, namely, for all (hko) reflections, $(h+k)$ and $(h-k)$ are divisible by 4, although these are not necessary space-group conditions.

(b) Intensities of reflections from (hko) and corresponding $(h\bar{k}o)$ planes in certain pairs of such reflections were found to be appreciably different. This is untenable for an orthorhombic crystal where (hko) and $(h\bar{k}o)$ are equivalent planes.

After obtaining the electron map as projected on (001) planes, a second projection was attempted on (010) plane and in order to obtain agreement in corresponding F-values, trials were carried out on the basis of molecular orientation as obtained by magnetic measurements by Banerjee (1938) But the equivalent positions required by the assumed space-group or even any other possible alternative space-group under the orthorhombic system could not be fitted in with the results obtained in the second projection. This led to suspect the correctness of the space-group.

In an attempt to see whether the (001) face is centred or not, a rotation photograph was taken around a diagonal axis [110] and the fundamental translation along that direction was found to be half of the diagonal distance in one photograph, while for a different setting of the crystal for a similar rotation photograph, the fundamental translation was found to be only quarter of the diagonal distance. The difference being surprising, the settings of the crystals were carefully checked up and fresh sets of rotation photographs were taken and it was finally concluded beyond doubt that rotation photographs round [110] and [1̄10] were different and gave the two types of photographs mentioned above. The two rotation photographs are reproduced in Plates XIVA and XIVB. Had the crystal been orthorhombic, the two
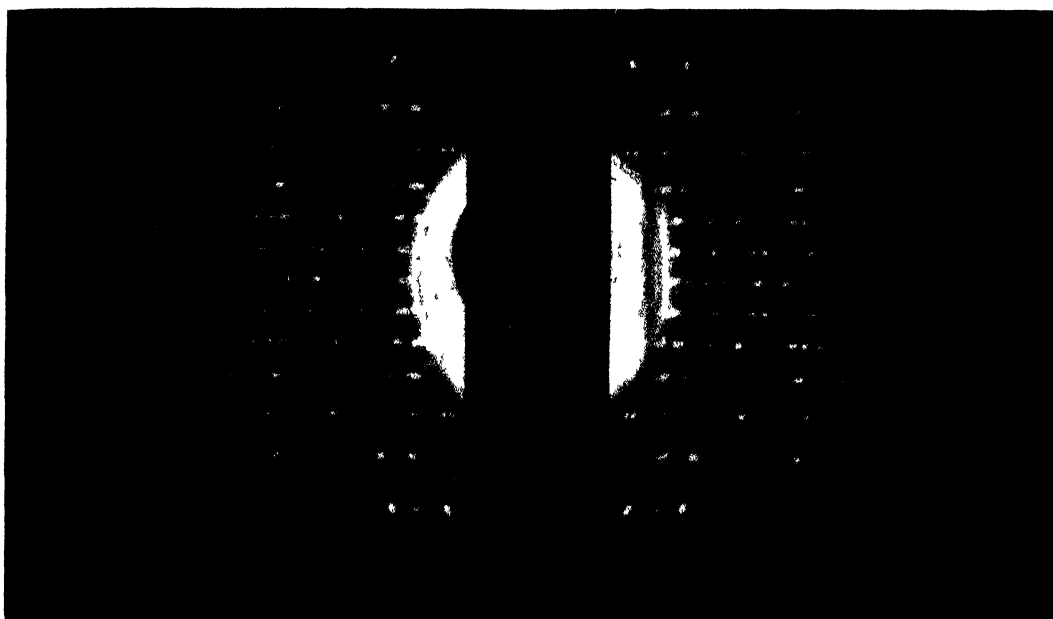
Rotation photograph round [ 110 ] on the orthorhombic notation
i.e, round $a$-axis of monoclinic cell       $a = 15\,85$ A
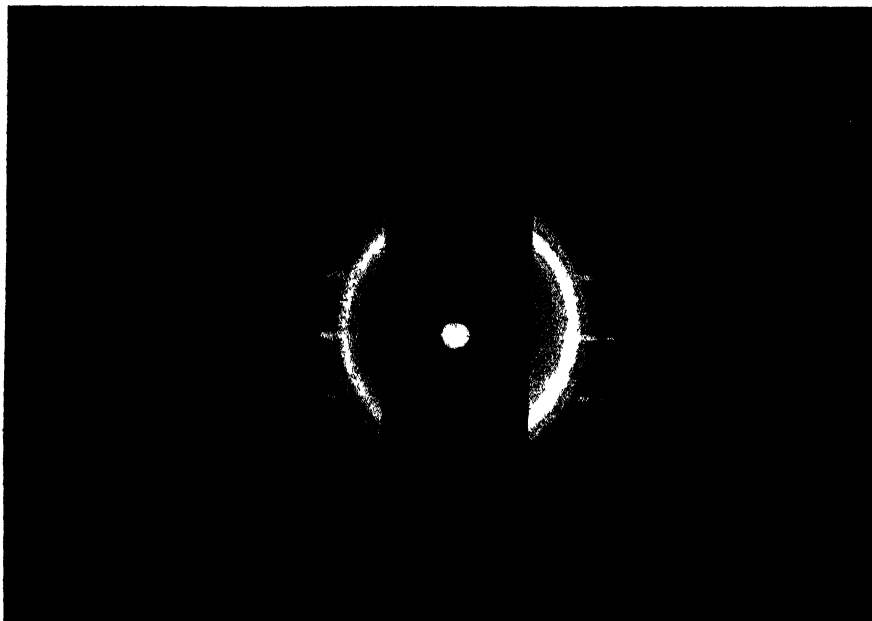
Rotation photograph round [ 110 ] on the orthorhombic notation i e round c-axis of monoclinic cell ( c=7 92 A )



Powder photograph of a mixture of anthraquinone and aluminium.

rotation photographs round the diagonal axes [110] and [1$\bar{1}$0] would have been identical. The striking difference observed is sufficient to prove beyond doubt that the crystal cannot be orthorhombic as concluded by the earlier workers. The elementary translations in these two diagonal directions come out as 15.85Å and 7 92Å respectively, which are more fundamental than the translations 19.68Å and 24.59Å along the directions ($a$ and $b$) that have been so far assumed to be the axial direction under the orthorhombic system. Taking into consideration the molecular arrangements already obtained by Fourier projections, it was found that the observed facts could be well accounted for by the arrangements of molecule in the old $ab$-plane as shown in Fig. 1 below :—
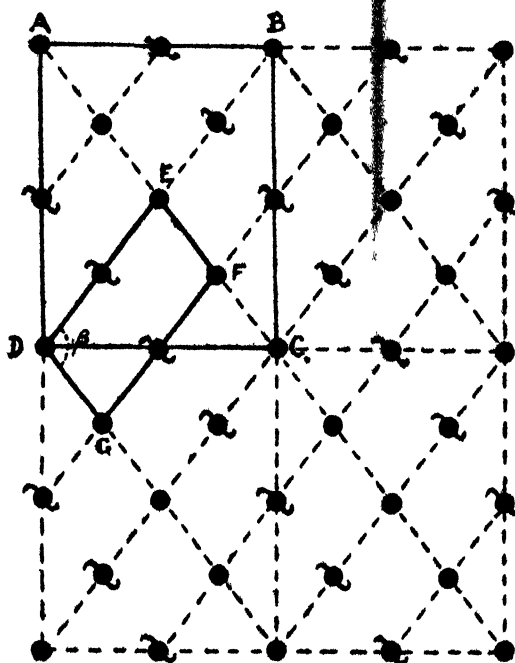


FIG. 1

Molecular net as projected on $ab$-plane

ABCD represents the old $ab$-face of the cell, DEFG is the correct fundamental unit cell (monoclinic) whose elements are $a = 15$ 85 Å, $b = 3.98$Å, $c = 7.92$ Å and $\beta = 102°/43'$, $c$-axis of the old system being the $b$-axis of the new system. The pseudo-orthorhombic character of the crystal has been really due to the accidental circumstance that 15.85 is approximately double of 7.92. The arrangement of molecule as shown in Fig. 1 accounts for the confusion of the earlier workers. The molecules represented by the symbol ' $\natural$ ' have their centres in planes $c/2$ (referred to old orthorhombic cell) above and below those of the molecules represented by shaded circles.

## Goniometric measurements

By careful goniometric measurements of all the faces by a Czapski two-circle theodolite goniometer, the old interfacial angles were re-measured in a laige number of crystals: and it was attempted to see whether X-ray evidence is corroborated in the development of crystal faces. A sketch of the anthraquinone crystal with its faces which commonly develop, as observed in the specimens crystallised from benzene, is shown in Fig. 2. The crystallographic data given under Table I (axial ratios being taken from X-ray measurements) revises the old values given by Groth under orthorhombic nomenclatures. It may be mentioned that the observed faces $a$, $c$, $m$, $y$ and $z$ (vide Fig. 2) correspond to $m$, $m$, $b$, $y$ and $x$ faces of Groth's data respectively and that the faces $b$, $n$, and $d$ recorded by Groth have not been observed at all, while the observed face $z$ was not included in Groth's data.
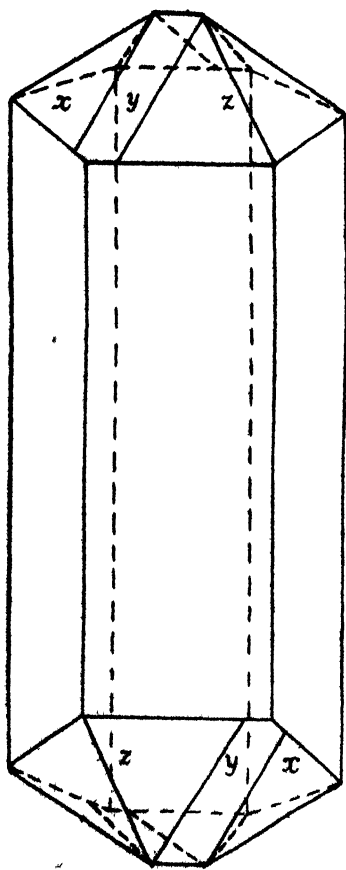


FIG. 2

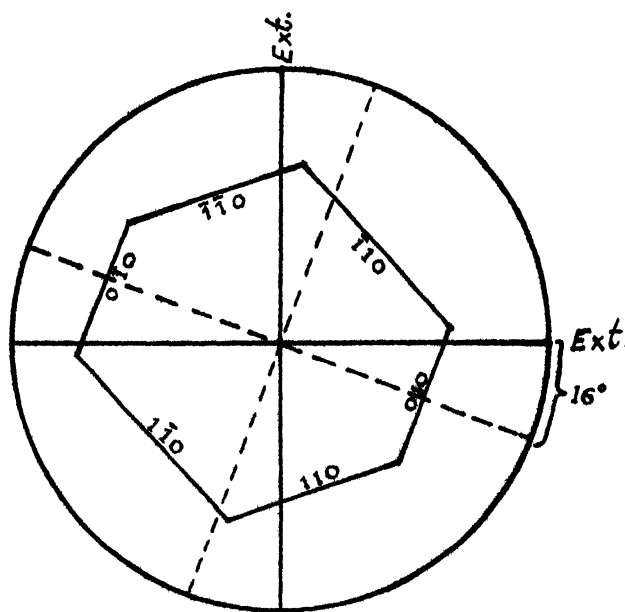Anthraquinone crystal with commonly developed faces.

FIG. 2a

Extinction directions in section of anthraquinone crystal crt perpendicular to symmetry axis (old $c$-axis)

TABLE I

| Faces | New Indices | Calculated | Observed |
|-------|-------------|------------|----------|
| $a : c$ | (100) : (001) | ... | $77°17'$ |
| $c : m$ | (001) : $(\bar{2}01)$ | $51°20'$ | $51°14'$ |
| $m : a$ | $(2\bar{0}1)$ : (100) | $51°22'$ | $51°29'$ |
| $a : x$ | (100) : (110) | $75°34'$ | $75°40'$ |
| $c : z$ | (001) : (011) | $62°45'$ | $62°45'$ |
| $x : z$ | (110) : (011) | $27°36'$ | $27°36'$ |
| $y : z$ | (111) : (011) | $12°30'$ | $12°37'$ |

It will be seen that the *a*- and *c*-faces of the crystal on the monoclinic nomenclature are the (110) and ($1\bar{1}0$) faces of the old orthorhombic system. Had the crystal been orthorhombic, its (110) and ($1\bar{1}0$) faces would have been identical planes. It would thus appear difficult to distinguish the new *a*- and *c*-faces of the crystal by goniometric measurement. But the existence of the top faces *x* and *z* which develop adjacent to the *a*- and *c*-faces at angles $75°40'$ and $62°45'$ respectively permit identification of the new *a*- and *c*-faces and the corresponding new axes without difficulty. The slight difference of the order of 10 to 15 minutes observed between the interfacial angles *a : m* and *c : m* is also found to be fairly consistent in the large number of crystals which have been examined under the goniometer and hence this difference can also be used as confirmation in identifying the *a*- and *c*-faces.

*Optical measurements*

With a view to obtain a further confirmation in respect of the monoclinic nature of the anthraquinone crystal, the optical extinction directions were determined by examining a section of the crystal cut parallel to the symmetry plane (*i.e.*, old 001 plane) under the polarising microscope. It was definitely found that the extinction directions in the *ab*-plane of the old system of axes make angles of about 16° with the *a*- and *b*-axes thus confirming the monoclinic character of the crystal. A number of similar crystal sections were examined under the polarising microscope and the mean deviation of the extinction direction from the old *a*- and *b*-axes worked out to be about 16°.

Dutta (1947) has measured the refractive indices of anthraquinone crystal along its principal directions. The relative values of the indices measured by Dutta are in agreement with the structure derived by the author.

### Revision of the Space group

The new unit cell contains 2 molecules instead of 8 in the old orthorhombic cell. Thus the previous unit cell being much bigger than the correct fundamental cell, the absent spectra showed symmetries greater than those required by any of the orthorhombic space groups. If $(hkl)$ represents the indices of a plane in the older orthorhombic notation, it can be easily shown that its equivalent indices $(HKL)$ referred to the new monoclinic axes are given by $H = (h+k)/2$, $K = 1$ and $L = (h-k)/4$. The conditions of absent spectra observed in the orthorhombic cell are thus modified as explained below :—

> (1)    $(h+k)$ and $(h-k)$ divisible by 4 for $hko$ planes reduce to ' H even for HOL planes '

and    (2)    (oo1) planes halved reduce to (OKO) halved.

These are the absent spectra conditions for the monoclinic space group $C^5_{2h}(P^2_1/a)$, which is, therefore, the space group for anthraquinone.

The monoclinic space group $C^5_{2h}(P^2_1/a)$ requires 4 asymmetric molecules to complete the necessary symmetry but there are only two molecules in the unit cell. Hence if all the halvings found are true halvings, we must ascribe a centre of symmetry to the molecule of anthraquinone, which is the only possible molecular symmetry for this space group. The existence of such centre of symmetry in the anthraquinone molecule is also supported by the dipole moment measurements by Fischer and Rogowski (1939).

### Feeble forbidden spots observed in highly over-exposed photograph

In a highly over-exposed Weissenberg photograph about the symmetry axis (old $c$-axis), 4 or 5 extremely weak reflections were observed, which on identification revealed planes forbidden by the space group $C^5_{2h}(P^2_1/a)$. These planes are $\overline{7}10$, $7\overline{5}0$, $\overline{5}30$ and $3\overline{5}0$ on the orthorhombic system, which are equivalent to 302, 103, 102 and $\overline{1}02$ planes respectively on the monoclinic system. Taking these planes into consideration, the space group of anthraquinone can no longer be taken as $C^5_{2h}(P^2_1/a)$ in the strict sense of space group, but has to be taken as $C^2_2$ in the bispheroidal class. In that case, the molecule does not require any centre of symmetry. But the little deviation from the centro-symmetrical molecule, which would account for these few extremely weak reflections, which are several times weaker than the weakest reflection measured, would be definitely negligible. In fact, these weak reflections will absolutely have no contribution to the electron density maps. Negative result obtained in the dipole measurements (Fischer and Rogowski 1939) also proves that the molecule is at least very nearly centro-symmetrical. So far as the structure is concerned, $C^5_{2h}(P^2_1/a)$ can, therefore, be regarded as at least approximately the correct space group for all practical purposes.

## Crystal data

The revised crystal data for anthraquinone are summarised below:—

Anthraquinone : $C_{14}H_8O_2$; melting point $273°C$; density, calculated $1.419$ ($1.419-1.438$ given by Groth); crystallises in the holohedral class of the monoclinic system, $a = 15.85$ Å, $b = 3.98$ Å, $c = 7.92$ Å, $\beta = 102°.7$. Space group, $C^5_{2h}$ ($P^2_1/a$). Two molecules per unit cell. Molecular symmetry, centre. Volume of the unit cell $= 487$ Å³. Calculated absorption coefficient for Cu K$_\alpha$ rays. $\mu = 9.1$ per cm, Total number of electrons per unit cell $= F(000) = 216$.

### DETERMINATION OF STRUCTURE FACTORS

*Photometry of spots in Weissenberg photographs and relative intensity measurements*

The relative intensity measurements were made by Zeiss photoelectric recording photometer. The method followed is briefly described below :—

The Weissenberg photo film was mounted on the object carriage of the photometer. The dimensions of the spots (Weissenberg photograph) whose intensities were to be measured were generally of the order of 2 m.m. × 1 mm. or smaller. The spot of light of the photometer was adjusted to be much smaller in dimension, about 0.5 mm. × 0.2 mm., and was first adjusted at one end of the spot under measurement. When the motor is started to take a record, the spot of light moves along its width while the transmitted light falls on the photoelectric cell. The current through the photoelectric cell produces deflection of the fibre of a string electrometer. The fibre is illuminated by a lamp and its movement is photographically recorded. The spot under measurement was then displaced along its length through a distance of 0.5 mm., small compared to the length by the lateral movement of the object carriage and the recording was repeated by allowing the spot of light to traverse the reflection spot again along its width. In this way each spot was scanned by the light spot completely by a number of traversals. The photometer was worked with the same sensitivity, that is, with the same range of the electrometer fibre between the " zero " position (direct beam of light falling into the photo-electric cell) and the " maximum blackening " position (beam of light completely cut off). This was done by noticing the movement of the fibre against a graduated scale in the view-finder and fixing its range by adjustment of the aperture through which the light falls into the photo-cell.

The actual intensity corresponding to any spot is not linearly proportional to the deflection of the electrometer fibre of the photometer. To obtain the integrated intensity, therefore, the amplitudes or the ordinates of the photometric curve are to be compared with a standard prepared according to Robinson's (1933) method.

The zero intensity line in the photometric record was drawn for each scanning of the Weissenberg spot. The zero line being taken as the abscissae, ordinates were drawn and measured at intervals of one millimeter. This can be quite easily done by placing a semi-transparent millimeter graph paper on the photo-metric records and reading off the ordinates. Each ordinate was matched with equivalent ordinates of the standard intensity curve, the abscissae corresponding to the latter being proportional to the intensity represented by the ordinate. All these abscissa for all the scannings of the spot were summed up, the net sum giving a relative measure of the integrated intensity.

### Reflections at small angles

The spot in the Weissenberg photograph having the smallest angle of diffraction was the 040 reflection. Reflections from planes of larger spacing, *i.e.*, smaller angle of diffraction are obstructed by the lead stop in the Weissenberg camera used to receive and absorb the direct X-ray beam. It was found, as can be seen from the space group condition as well, that 220 and 2̄20 are the only such planes. It was, therefore, necessary to measure their intensities for inclusion in the Fourier summation. This was done by taking separate oscillation photograph in another camera in which the lead stop used to receive the direct beam was made of such small dimension as to allow the 220 reflection to be photographed. The oscillation ranges were so adjusted that 220 and 260 reflections were recorded in one oscillation photograph and 2̄20 and 2̄60 in another. The relative integrated intensities of these pairs of reflections were measured in the same way as in the case of Weissenberg reflections.

### Absolute intensity measurements

In order to calculate the absolute structure factors of the reflecting planes, it is necessary to convert the relative integrated intensities obtained from Weissenberg photographs into absolute scale. For this purpose a powder photograph was taken with a mixture of anthraquinone and aluminium and the intensities of anthraquinone lines were compared with those of aluminium, the latter being absolutely known from the measurements by Brindley (1936). The scattering power and absorption co-efficient of aluminium being much greater than those of anthraquinone, the powder mixture was prepared with 1 part of aluminium and 6 parts of anthraquinone by weight in order that the intensities of reflections and the effective absorption co-efficients for the two ingradients might be comparable. The mixture was crushed into a fine powder in a mortar. The powder was made pasty by a little amount of solution of collodion in ether and formed into a stick by pushing the paste through a capillary tube. A filter of thin nickel foil was used to absorb the Cu-K radiation to avoid confusion among too many lines. The powder

photograph of the mixture is reproduced in plate XIV B. In order to dis-
tinguish the aluminium lines from those of the anthraquinone in the photo-
graph, a separate-powder photograph of anthraquinone alone was taken.
Relative intensities of the powder lines were measured exactly in the same
way as in the Weissenberg photograph but in this case the spot of light was
made longer but narrower and each line was scanned by the light spot once.
The relative integrated intensities of the different lines are given in Table II
below :—

TABLE II

| Substance | Reflecting planes | | Relative integrated intensity |
|---|---|---|---|
| Aluminium | 111 | 11.3 | Observed ratio = 2.38 |
| | 200 | 4 8 | Calculated ratio from Brindley's data = 2.22 |
| Anthraquinone ... | 220 | 18.6 | |
| | 040 | 6 8 | |

Hence out of the 111 and 200 reflections of aluminium, the former being
more intense was considered more reliable and used for final comparison with
anthraquinone lines. 3 prominent anthraquinone lines were obtained in the
powder photograph, viz. (1) 220 plane, i.e., superposition of 220, $\overline{2}20$, $2\overline{2}0$
and $\overline{2}\overline{2}0$ planes ; (2) 040 planes, i.e., superposition of 040 and 0$\overline{4}$0 planes and
(3) superposition of 440, 260 and their derivatives with negative indices.
When the monoclinic nature of the anthraquinone crystal was established, it
was known that $hko$ and $h\overline{k}o$ planes are really different planes except for
axial planes and are generally of different intensities. Powder line obtained
by superposition of such planes, therefore, could not be made use of for
absolute intensity measurements. But the planes 040 and 0$\overline{4}$0 being equi-
valent - planes on the monoclinic system as well, the intensity of this line was
used for comparison with the 111 reflection of aluminium. Structure factor
for the latter was taken as 8.70 × 4 from Brindley's (1936) measurements.
The structure factor of 040 plane thus worked out to be 164.0 and on that
basis, the structure factors of other planes have been calculated from their
relative intensities in Weissenberg photographs. The details of calculation
and questions of absorption and extinction have been discussed in the fol-
lowing section of this chapter.

With a view to checking up the accuracy of the structure factor of 040
plane on which the absolute intensity measurements for all reflections have
been based, another powder photograph was taken with a mixture of anthra-
quinone and rock salt and by similar comparison of intensities, structure

factor of 040 plane worked out to be 166.0 as against 164.0 obtained from comparison with aluminium lines. The agreement happens to be unexpectedly satisfactory. In view of the probable error of $\pm 10\%$ in the intensity measurements and the error for not applying relative absorption corrections, which was comparatively larger in the case of rock salt-mixture, the above agreement appears to be somewhat accidental. Nevertheless, the agreement provides a confirmation that the value of $F_{040}$ obtained from the powder photograph is approximately correct.

*Evaluation of Absolute structure factors—Absorption and Extinction effects*

(a) *Powder photograph with mixture of anthraquinone and aluminium.*— The integrated intensity for a powder line (neglecting absorption) on cylindrical film is given by :

$$I = \tfrac{1}{16} \cdot \frac{N^2 e^4 \lambda^3 . l}{\pi m^2 c^4 . r} \cdot \frac{1 + \cos^2 2\theta}{\sin 2\theta . \sin \theta} \cdot p . F^2 . \partial V$$

$$= A . N^2 . \Theta . p . F^2 \partial V.$$

where $\quad A = \dfrac{e^4 . \lambda^3 . l.}{16 \pi m^2 c^4 r} = $ Constant for particular experiment.

$N = $ Number of unit cells per unit volume.

$$\Theta = \frac{1 + \cos^2 2\theta}{\sin 2\theta . \sin \theta}$$

$p = $ Number of equivalent planes.

$F = $ Structure factor.

Thus comparing integrated intensity of an anthraquinone line with that of an aluminium line in the powder photograph, we get

$$\frac{I_A}{I_{A'}} = \frac{N_A^2 . \Theta_A . p_A . F_A^2 . \partial V_A}{N_{A'}^2 . \Theta_{A'} . p_{A'} . F_{A'}^2 \partial V_{A'}}$$

where suffixes A and A′ denote corresponding values for the anthraquinone and aluminium lines respectively. As anthraquinone and aluminium were taken in the ratio 6 : 1 by weight for the powder stick,

$$\frac{\partial V_A}{\partial V_{A'}} = 6 . \frac{\rho_{A'}}{\rho_A} = 6 \times \frac{2.7}{1.42} = 11.4,$$

$\rho_{A'}$ and $\rho_A$ being the densities of aluminium and anthraquinone respectively. In the above equation therefore, $I_A/I_{A'}$ being measured and all other factors except $F_A$ being known, the absolute value of $F_A$ can be calculated. $F_A$ for c40 plane thus worked out to be 164.0.

- In the above calculation, no allowance has been made for the relative absorption effects for anthraquinone and aluminium in the powder rod.

The relative absorption effect was, however, reduced to minimum by taking the substances in suitable proportion and by using very thin powder rods. The calculated values of linear absorption co-efficients for anthraquinone and aluminium for copper $K_\alpha$ radiation are 9.1 and 131.6 per cm. respectively (calculated from mass absorption co-efficients of different atoms as given in the 'International Tables for the determination of crystal structure'). The proportion of anthraquinone and aluminium in the powder being 11.4 : 1 by volume, the effective absorption co-efficient are 8.4 and 10.6 respectively. The radius of the powder rod used was about 0.025 cm. The approximate probable error in integrated intensities and hence in F-values for 040 reflection of anthraquinone can be calculated from the Table given on page 584 of 'International Table for the determination of crystal structure.' This works out to be roughly +4%, which is small compared to probable limits of experimental error in intensity measurements.

(b) *Weissenberg rotation photograph.*—The appropriate formula for integrated intensity of reflection from a mosaic or ideally "imperfect" crystal may be written as :

$$I = \frac{N^2 e^4 \lambda^3}{4\mu m^2 c^4} \cdot \frac{1 + \cos^2 2\theta}{\sin 2\theta}. \quad F^* = A.\beta.F^2$$

where $\quad A = \dfrac{N^2 e^4 \lambda^3}{4\mu m^2 c^4} \quad$ and $\quad \beta = \dfrac{1 + \cos^2 2\theta}{\sin 2\theta}$

F(040) being determined absolutely from powder photograph, F-values for other reflections have been calculated from relative integrated intensity measurements of reflections in Weissenberg photograph, *i.e.*, from the relation

$$F^2 = \frac{I}{I_{010}} \cdot \frac{\beta_{010}}{\beta} \cdot F_0^2{}_{0}^{*}$$

assuming A, which is equal to $N^2 e^4 \lambda^3 / 4\mu m^2 c^4$, to be constant for all reflections. But A will be constant only if $\mu$ is constant. Variation of $\mu$ has, however, been neglected in view of the following considerations :—

The linear absorption co-efficient of anthraquinone (calc. $\mu = 9.1$) being fairly large, care was taken to ensure while taking the Weissenberg photographs that the specimens did not present greatly different paths to the beam in the different reflecting positions. This was done by selecting suitable crystal specimen for the different rotation photographs so as to provide fairly uniform cross-sections parallel to the rotation axes. Further, very small crystals weighing about 0.2 milligram were used to reduce non-uniformity of cross-section to the minimum. Relative absorption corrections were, therefore, not applied. With the small sizes of the crystals used, and further since it was found that the variation of crystal size did not have appreciable influence on intensities, extinction was considered to be small. No attempt has therefore been made to correct for the extinction.

*Structure factors measured and calculated*

The values of the structure factors in absolute units derived from integrated intensity measurements are given under "F measured" in Table III. The indices HKL of planes given in Table III refer to the old orthorhombic cell after Groth. As the Fourier summations were carried out in terms of the orthorhombic cell using the corresponding indices of the planes, these indices have been retained in Table III. Corresponding equivalent indices HKL referred to the new monoclinic axes are obtained from the general relations already given, namely, $H = (h + k)/2$, $K = 1$ and $L = (h - k)/4$. These new indices have also been included under the second column in Table III. Structure factors derived for the orthorhombic cell have, however, been divided by 4 in order to get the same in terms of the monoclinic cell. The latter values are given in Table III.

F (calculated) given under the last column in Table III have been calculated on the basis of co-ordinates of atoms as finally obtained from the electron maps. The values of atomic structure factors for carbon have been taken from Robertson's paper (1935) on the structure of benzoquinone. In the case of benzoquinone, Robertson considered that the existing oxygen $f$-curve would have to be modified by introducing a large temperature factor, and from the fact that peak value of electron density on the oxygen centre in his analysis was not found to be much higher than that for the carbon atoms, he assumed the average thermal movement of the oxygen atom to be of the same order as that of carbon atom. As such, the carbon $f$-curve was used by him for oxygen as well, after weighing in the ratio 8 to 6 in the analysis of benzoquinone. In the present analysis on anthraquinone, the peak value of electron density at the oxygen centre is found to be decidedly much higher than those for carbon atoms, actual values being 13.0 per sq. A.U. for oxygen and 7.5 to 9.0 per sq. A.U. for carbon atoms. In view of the uncertainty in the $f$-curve for oxygen atom, structure factors were separately calculated by using values used by Robertson as well as by those from the measuremants on MgO by Wollan (1930). As the latter gave a better agreement with the observed F-values for most of the reflections, Wollan's values have been preferred and corresponding values of F (calculated) are given in Table III. The general order of agreement between measured and calculated values of F is quite comparable to those obtained for other structures which have been successfully analysed. Considering the uncertainty in the $f$-curve for oxygen and the fact that contributions of the 16 hydrogen atoms in the new cell (monoclinic) have not been separately accounted for, the discrepancies appear to be well within the limits of experimental error.

*The preliminary estimate of the structure*

· . With a view to obtaining the correct signs of the co-efficients $F(hkl)$ of the Fourier series, a preliminary analysis of structure by the trial and error method

Table III

Measured and calculated values of structure factor.

| hkl (after Groth) | HKL (referred to monoclinic cell) | F measured | F calculated | hkl (after Groth) | HKL (referred to monoclinic cell) | F measured | F calculated |
|---|---|---|---|---|---|---|---|
| 002 | 020 | • 13 | +14 | 4(24)o | (14)o5 | 6 | −5 |
| 400 | 201 | 11 | − 2 | 4(2̄4)o | (ī0)o7 | 6 | − 6 |
| 800 | 402 | 20 | +21 | 4(28)o | (16)06 | 5 | + 7 |
| (12)oo | 603 | 25 | +23 | 4(2̄8)o | (ī2)o8 | 5 | + 7 |
| (16)oo | 804 | 2| | +21 | 620 | 401 | 22 | +16 |
| (20)oo | (10)o5 | 10 | +10 | 62o | 202 | 27 | +23 |
| 040 | 2ı1 | 41 | +36 | 66o | 600 | 4 | − 7 |
| 080 | 4̄02 | 27 | −14 | 660 | 003 | 13 | −13 |
| o(12)o | 6̄03 | 19 | −33 | 6(10)o | 8oı | 15 | +18 |
| o(16)o | 8o4̄ | 12 | −11 | 6(ī0)o | 2̄04 | 11 | +15 |
| o(24)o | (12)o6̄ | 21 | −19 | 6(14)o | (10)o2̄ | 16 | −19 |
| 220 | 200 | 35 | +32 | 6(ī4)o | 405 | 13 | −15 |
| 2̄20 | 001 | 35 | +29 | 6(18)o | (12)o3̄ | 6 | + 2 |
| 260 | 40ı | 30 | −27 | 6(ī8)o | 6̄06 | 17 | + 9 |
| 2̄6o | 2̄02 | 32 | −29 | 6(22)o | (14)o4̄ | 10 | −10 |
| 2(10)o | 6̄o2 | 3 | + 4 | 6(26)o | (16)o5̄ | 4 | + 3 |
| 2(ī0)o | 4̄03 | 1| | +14 | 840 | 6o1 | 55 | −40 |
| 2(14)o | 8o3̄ | 26 | −18 | 840 | 203 | 54 | −39 |
| 2(ī4)o | 6̄o4 | 14 | −11 | 880 | 8oo | 15 | −11 |
| 2(18)o | (10)o4̄ | 13 | +13 | 8̄8o | 004 | 27 | −20 |
| 2(ī8)o | 8̄05 | 16 | +16 | 8(16)o | (12)o2̄ | 25 | +19 |
| 2(22)o | (12)o5̄ | 15 | −11 | 8(ī6)o | 4̄06 | 31 | +24 |
| 2(2̄2)o | (ī0)06 | 10 | − 5 | 8(2o)o | (14)o3̄ | 16 | +14 |
| 2(26)o | (14)o6̄ | 5 | − 4 | 8(2̄0)o | 6̄07 | 27 | +25 |
| 440 | 400 | 40 | −40 | 8(24)o | (16)o4 | 7 | − 8 |
| 4̄40 | 002 | 40 | −39 | 8(2̄4)o | ⸱ 8o8 | 6 | − 6 |
| 480 | 6oı | 26 | +25 | 8(2̄8)o | (10)o9 | 3 | − 2 |
| 4̄8o | 2̄03 | 30 | +25 | (10)2o | 6̄02 | 9 | − 6 |
| 4(12)o | 8o2̄ | 4 | + 5 | (10)6o | 8o1 | 47 | −31 |
| 4(16)o | (10)o3̄ | 6 | o | (10)6̄0 | 204 | 44 | −31 |

## Table III (*contd.*)
### Measured and calculated values of structure factor.

| hkl (after Groth) | HKL (referred to monoclinic cell) | F measured | F calculated | hkl (after Groth) | HKL (referred to monoclinic cell) | F measured | F calculated |
|---|---|---|---|---|---|---|---|
| (10) (14)o | (12)o$\bar{1}$ | 18 | + 8 | (22) (10)o | (16)o3 | 4 | + 7 |
| (10) ($\bar{1}\bar{4}$)o | $\bar{2}$o6 | 5 | − 2 | o41 | 2$\bar{1}\bar{1}$ | 2 | − 2 |
| (10) (18)o | (14)o$\bar{2}$ | 33 | +31 | o42 | 2$\bar{2}\bar{1}$ | 10 | −11 |
| (10) ($\bar{1}\bar{8}$)o | $\bar{4}$o7 | 21 | +20 | o43 | 23$\bar{1}$ | 4 | − 5 |
| (10) (26)o | (13)o$\bar{4}$ | 6 | − 4 | o44 | 24$\bar{1}$ | 8 | − 8 |
| (10) ($\bar{2}\bar{6}$)o | 8o9 | 3 | − 3 | o81 | 4$\bar{1}\bar{2}$ | 1 | + 2 |
| (12)4o | 8o2 | 6 | − 9 | o82 | 4$\bar{2}\bar{2}$ | 13 | +16 |
| (12)8o | (10)10 | 9 | +10 | o83 | 4$\bar{3}\bar{2}$ | 5 | + 7 |
| (12)8̄o | 205 | 11 | + 11 | o84 | 4$\bar{4}\bar{2}$ | 7 | − 3 |
| (12) (16)o | (14)o$\bar{1}$ | 4 | − 4 | o(12)1 | 6$\bar{1}\bar{3}$ | 7 | − 7 |
| (12) ($\bar{1}\bar{6}$)o | 2o7 | 6 | −11 | o(12)2 | 6$\bar{2}\bar{3}$ | 1 | o |
| (12) (24)o | (18)o$\bar{3}$ | 6 | − 7 | o(12)4 | 6$\bar{4}\bar{3}$ | 3 | + 1 |
| (12) ($\bar{2}\bar{4}$)o | 6o9 | 4 | − 7 | o(16)2 | 8$\bar{2}\bar{4}$ | 2 | − 7 |
| (14)2o | 8o3 | 5 | − 6 | o(16)3 | 8$\bar{3}\bar{4}$ | 2 | + 3 |
| (14)$\bar{6}$o | 4o5 | 6 | − 9 | o(16)4 | 8$\bar{4}\bar{4}$ | 10 | + 7 |
| (14) (10)o | (12)o1 | 9 | +14 | o(20)3 | (10)$\bar{3}\bar{5}$ | 6 | − 8 |
| (14) ($\bar{1}\bar{0}$)o | 2o6 | 6 | +14 | o(24)1 | (12)$\bar{1}\bar{6}$ | 3 | − 2 |
| (14) (14)o | (14)oo | 9 | − 9 | o(24)2 | (12)$\bar{2}\bar{6}$ | 3 | − 5 |
| (14) ($\bar{1}\bar{4}$)o | oo7 | 5 | − 7 | o(28)2 | (14)$\bar{2}\bar{7}$ | 3 | + 5 |
| (14) ($\bar{1}\bar{8}$)o | $\bar{2}$o8 | 4 | + 6 | 401 | 21$\bar{1}$ | 34 | −17 |
| (14) (22)o | (18)o$\bar{2}$ | 6 | − 6 | 402 | 22$\bar{1}$ | 43 | +32 |
| (16) ($\bar{1}\bar{2}$)o | 2o7 | 8 | − 4 | 403 | 2$\bar{3}$ | 11 | + 7 |
| (18)2o | (10)o4 | 24 | +18 | 8o1 | 4$\bar{1}\bar{2}$ | 9 | − 1 |
| (18)$\bar{2}$o | 8o5 | 28 | +26 | 8o2 | 4$\bar{2}\bar{2}$ | 5 | + 7 |
| (18) (10)o | (14)o2 | 11 | − 4 | 8o3 | 4$\bar{3}\bar{2}$ | 21 | −10 |
| (18) ($\bar{1}\bar{0}$)o | 4o7 | 7 | o | 8o4 | 4$\bar{4}\bar{2}$ | 15 | +12 |
| (18) (14)o | (16)o1 | 9 | −12 | (12)o2 | 6$\bar{2}\bar{3}$ | 26 | +25 |
| (18) ($\bar{1}\bar{4}$)o | $\bar{2}$o8 | 9 | −12 | (12)o3 | 6$\bar{3}\bar{3}$ | 12 | + 5 |
| (20) (12)o | (16)o2 | 5 | − 4 | (16)o1 | 8$\bar{1}\bar{4}$ | 24 | +13 |
| (22)2o | (12)o5 | 6 | − 6 | (20)o1 | (10)$\bar{1}\bar{5}$ | 19 | −12 |
| (22)$\bar{2}$o | (10)o6 | 5 | − 2 | | | | |

was undertaken. The following points rendered useful guidance to arrive at a tentative structure for the purpose :—

1. Considering the known form of anthracene molecule consisting of three plane hexagonal rings lying in one plane, the anthraquinone molecule derived by adding two oxygen atoms at the central ring of anthracene was also considered to be planar in structure to start with. The probability of such a planar structure of anthraquinone molecule was also supported by the analogous structure of benzoquinone already analysed by Robertson where the planar structure of the benzene ring has not been disturbed by the addition of the two oxygen atoms.

2. The anthraquinone molecule was assumed to be centro-symmetrical as required by the space group condition and also supported by the dipole measurement (Fischer and Rogowski, 1939).

3. In view of the small dimension of $3.68$ Å only along $c$-axis of the old unit cell, it would be difficult to accommodate the molecule in the cell if the molecular plane is very much tilted from the $ab$-face.

4. Although there are 8 molecules in the pseudo-orthorhombic cell, the real unit cell finally obtained under the monoclinic system contains 2 molecules only, where the second molecule is derived from the first by the symmetry operation. As the molecule has got a pseudo-centre of symmetry, a knowledge of the position of atoms comprising half of one molecule only is sufficient to build up the entire structure. The problem thus gets much simplified as the same reduces to the determination of parameters for 7 carbon atoms and one oxygen atom only.

5. For the preliminary trials, all the three benzene rings of anthra-quinone molecule were assumed to be regular hexagons as in the case of anthracene. The dimensions of the rings were also assumed to be similar to those observed in anthracene and benzoquinone.

Taking the above points into consideration, it was then tried to find the $x$ and $y$ co-ordinates of the different atoms in the molecule which would give the calculated structure factors as close a fit with the experimental F values as was possible. After a few trials, the following structure gave sufficiently reasonable agreement to obtain the signs of the $F(hko)$ co-efficients for the Fourier summation.

It was concluded by Banerjee (1938) from his magnetic measurements on this crystal that the molecular plane is tilted about the $b$-axis from the $ab$-plane by 30°. This was taken as the starting point for the trial structures for the Fourier projection along the other two axes. The $x$ and $y$ co-ordinates being already known accurately from $c$-axis projection, the $z$-co-ordinates for the purpose of trials were calculated from the above tilt of molecular plane about the $b$-axis.
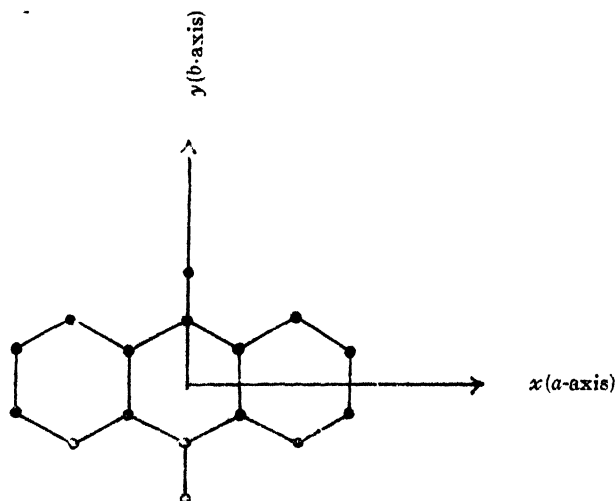
## Fourier Summations

Fourier syntheses weie carried for projections on the pseudo-orthorhombic planes as they gave much clearer resolutions than the real monoclinic planes. Crystallographic axes, co-ordinates of atoms, molecular orientations, etc., detailed hereafter are as referred to the pseudo-orthorhombic cell $(a = 19.68\text{Å}, b = 24.59\text{ Å}$ and $c = 3.98\text{Å})$ containing 8 molecules of anthraquinone. Corresponding values with reference to the monoclinic cell can easily be calculated from those obtained for this enlarged cell.

A large number of reflecting planes were taken into account in the Fourier projections, particularly along the old $c$-axis. Contributions from about 180 $(hko)$ planes $(i.e.,$ new $hol$ planes) were summed up in the case of $c$-axis projection as against the maximum of about 150 and 130 planes for one of the projections in the case of anthracene and benzoquinone respectively. Integrated intensities were measured over a wide range, the most intense one having an integrated intensity of about a thousand times that of the weakest. Intensities of a few still weaker reflections were estimated visually from a highly over-exposed photograph and included in the Fourier summation. In the $c$-axis projection, the Fourier summation was carried out at subdivisions of $a/48$ and $b/48$, which are equivalent to $0.410$ Å along $a$-axis and $0.512$ Å along $b$-axis respectively. For accurate location of the atomic centres, additional summations at closer intervals with axial subdivisions of $a/96$ and $b/96$ round about the atomic centres $(i.e.,$ at intervals of $0.205$ Å and $0.256$ Å along $a$- and $b$-axes respectively) were carried out. Axial subdivisions in the projections along $a$- and $b$-axes were $b/48$, $c/12$ and $a/48$, $c/12$ respectively, where $c/12 = 0.332$ Å. Closer summations in the regions of the atoms were carried out in these projections also.

### Electron maps and atomic co-ordinates

The contour maps were drawn by the graphical interpolation from the summation totals. The maps are reproduced in Figs. 3, 5 and 7. Separate diagrams showing how the molecules are arranged in the projections along the 3 axes are given in Figs. 4, 6 and 8. All the atoms in the molecule are remarkably well resolved in the c-axis projection, whereas in the other two projections, atomic centres can hardly be fixed with accuracy owing to considerable overlapping of atoms. x and y co-ordinates have, therefore, been taken from the c-axis projection alone, using the other two projections merely as a general check. The accuracy of the co-ordinates is in general 0.01 Å. Direct determination of the z-co-ordinates from the a- and b-axes projections would be
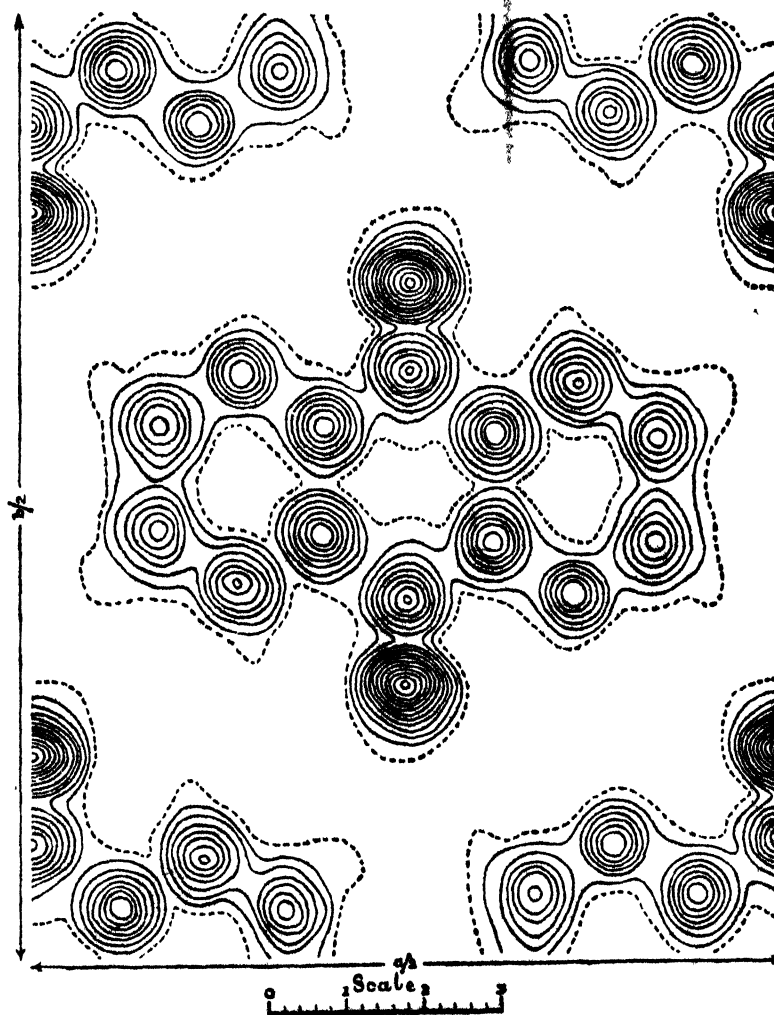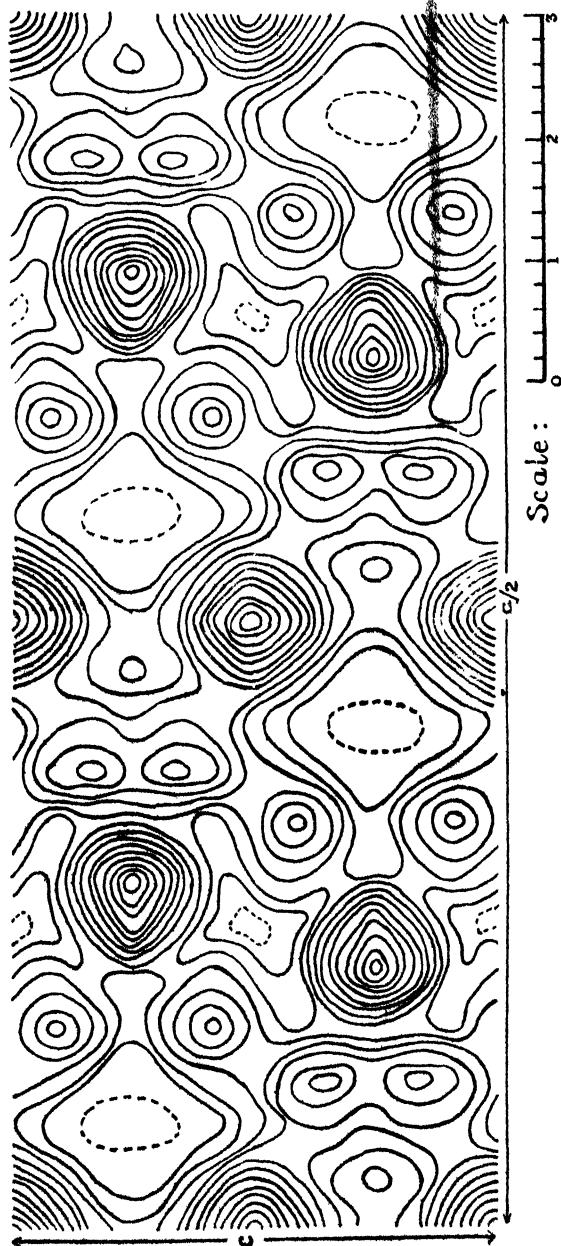


FIG. 3

Projection along the old c-axis. Contour lines drawn at intervals of one electron per A², the one electron line being dotted.

unreliable owing to overlapping of atoms. In *b*-axis projection, the molecular plane is found to be tilted from (oor) plane by 27° degrees about the *b*-axis (30° degrees, found by magnetic measurements). The fact that the centres of atoms in one molecule lie approximately on a line in the *b*-axis projection supports the planar structure of the molecule, as has also been found in other allied aromatic compounds. In *a*-axis projection, the oxygen atom and the connecting carbon atom are well resolved, which permit independent evaluation of the co-ordinates for those atoms. In both *a*- and the *c*-axes projections, the oxygen and the adjoining carbon atom and the centre of the molecule lie on the same straight line, which indicates that the oxygen atoms also lie in the plane of the rings. From these considerations, the planar structure of the molecule has been concluded. Deviation from the planar structure,
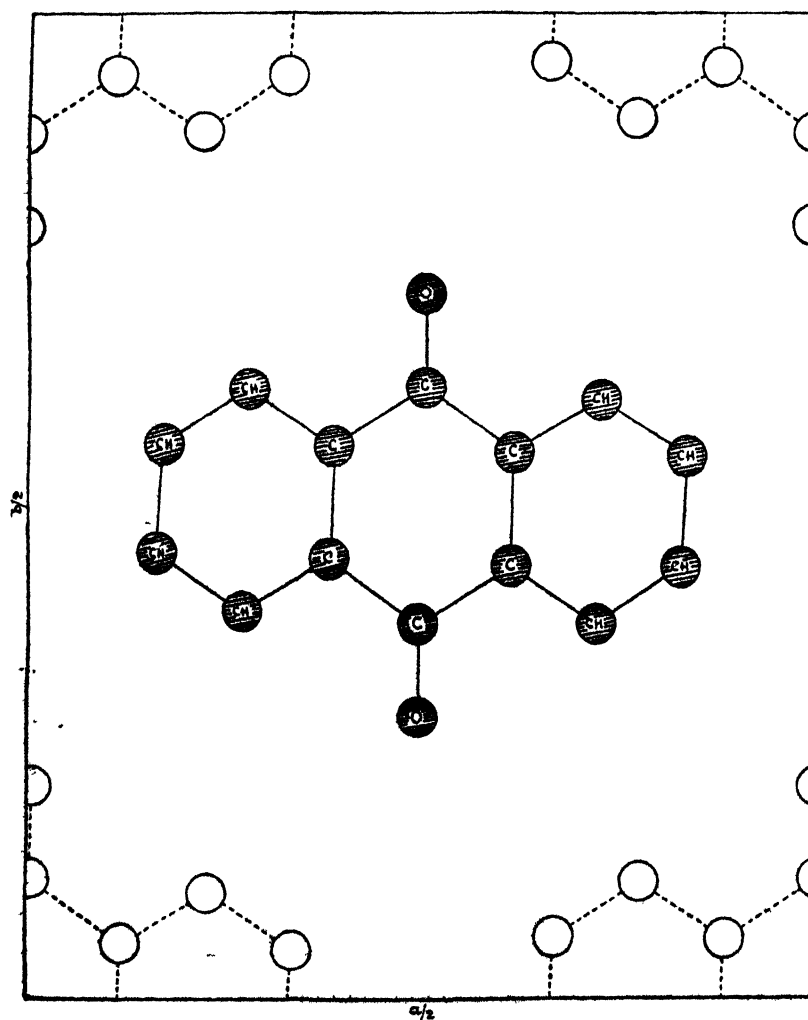


FIG. 4 .

Showing how the molecules are grouped in *c*-axis projection.

if any, is believed to be negligible. $z$ co-ordinates have, therefore, been worked out from the relation $z = lx + my$, where $l = \tan 27°$ and the constant '$m$' is calculated to be 0.0493 from the oxygen co-ordinates assigned independently in the $a$- and the $c$-axes projections. The co-ordinates with reference to the orthorhombic cell are given in Table IV. On transformation of the orthorhombic axes of co-ordinates to those of the new monoclinic cell, the final co-ordinates referred to the monoclinic system of axes are obtained from the following relations :—



Fig. 5

Projection along the old $b$-axis. Contour lines drawn at intervals of one electron per A², the one electron line being dotted.

Scale :

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$$x'/a' = x/a + y/b \quad \cdots \quad \cdots \quad \cdots \quad \cdots \quad (i)$$

$$y'/b' = z/c \quad \cdots \quad \cdots \quad \cdots \quad \cdots \quad (ii)$$

$$z'/c' = 2(x/a - y/b) \quad \cdots \quad \cdots \quad \cdots \quad \cdots \quad (iii)$$

$x'y'z'$ and $xyz$ are equivalent co-ordinates on the monoclinic and orthorhombic system and $a'b'c'$ and $a, b, c$ are the corresponding axial lengths of the two cells respectively. The final co-ordinates referred to the monoclinic cell are given in Table V.
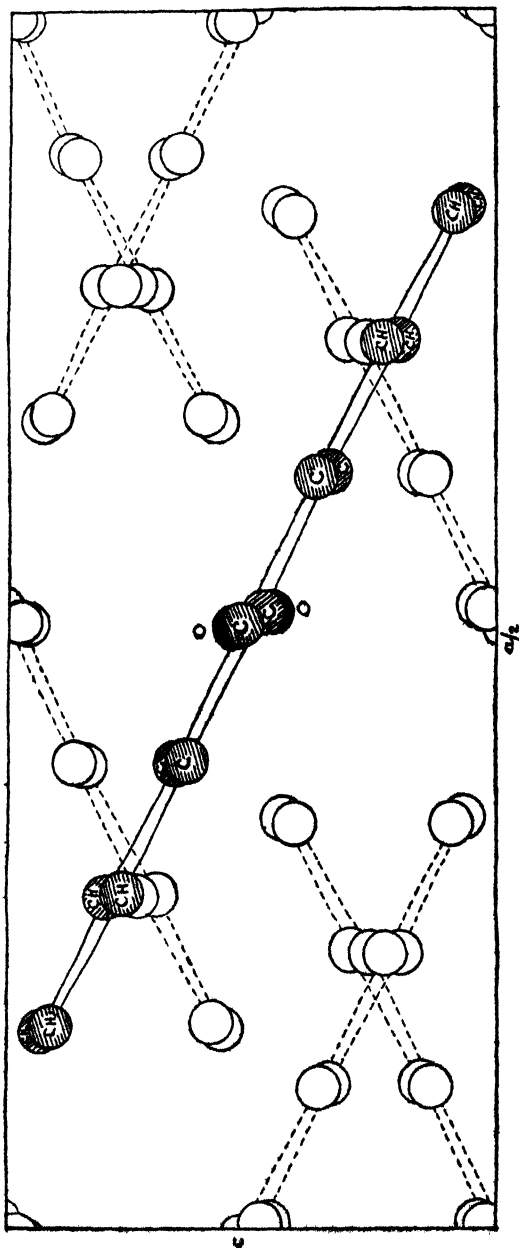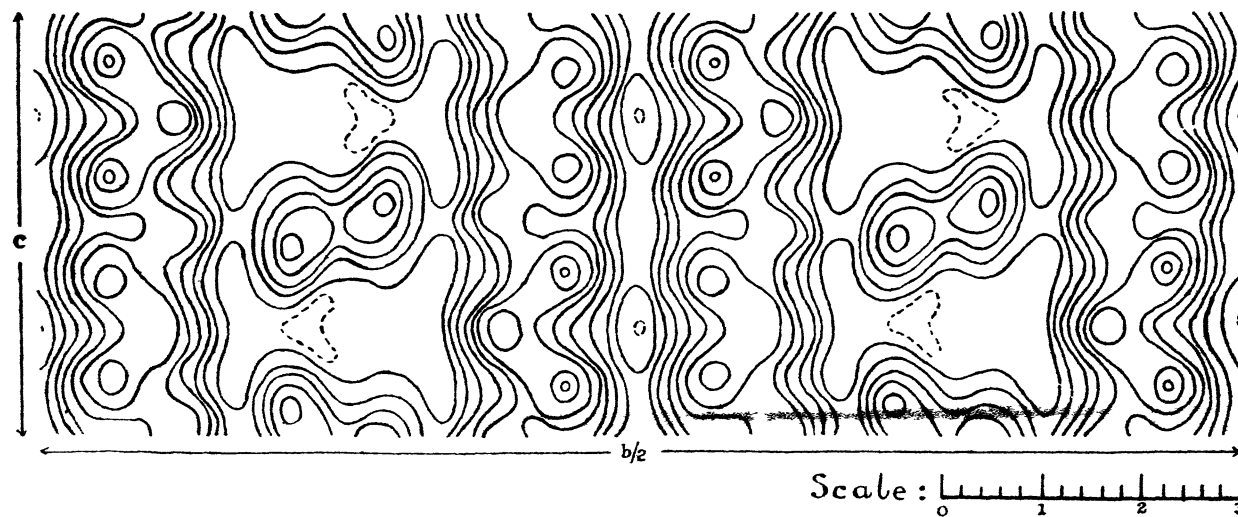


FIG. 6

Showing how the molecules are arranged in b-axis projection.

FIG. 7

Projection along the old a-axis. Contour lines drawn at intervals of one electron per A², the one-electron line being dotted
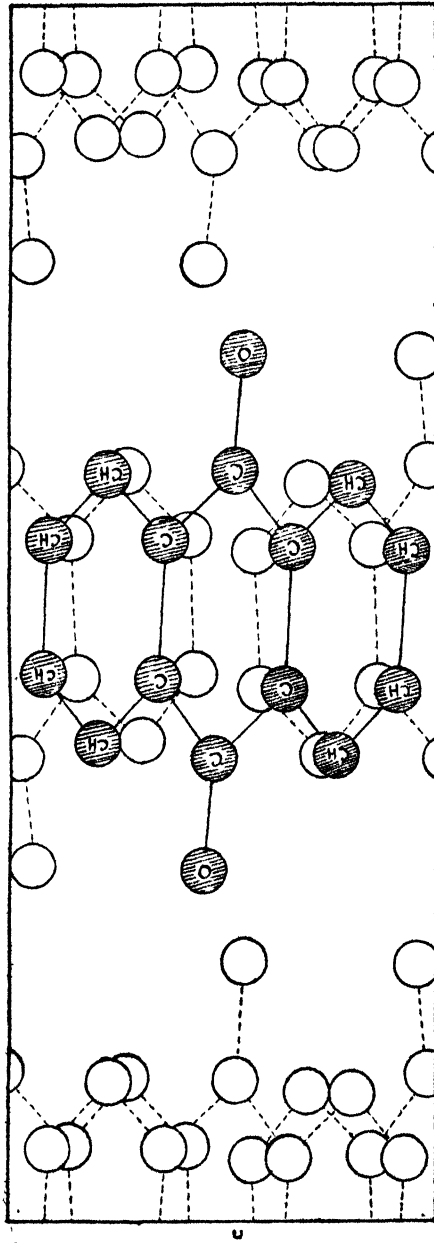
Fig. 8

Showing how the molecules are grouped in a-axis projection.

## TABLE IV

Co-ordinates of atoms referred to orthorhombic cell. Molecular centre of symmetry at (ooo) as origin

| Atom (vide Fig. 9) | xÅ | (2πx/a)° | yÅ | (2πy/b)° | zÅ | (2πz/c)° |
|---|---|---|---|---|---|---|
| A (CH) | −3.253 | −50.3 | 0 765 | 11.2 | −1.634 | −147.8 |
| B (CH) | −2.198 | −40.2 | 1.447 | 11.2 | −1 059 | − 95.8 |
| C (C) | −1.115 | −20.1 | 0.745 | 0.9 | −0.536 | −48.5 |
| D (C) | 0.038 | 0.7 | 1 476 | 1.6 | 0 092 | 8.3 |
| E (C) | 1.164 | 21.3 | 0.649 | 9.5 | 0.630 | 57.0 |
| F (CH) | 2.236 | 40.9 | 1 311 | 9.2 | 1.214 | 109.5 |
| G (CH) | 3.308 | 60.3 | 0.615 | 8.8 | 1.730 | 156 6 |
| H (O) | 0.049 | 0.9 | 2.623 | 8.4 | 0.155 | 14.0 |

## TABLE V

Co-ordinates of atoms referred to monoclinic cell. Molecular centre of symmetry at (ooo) as origin

| Atom (vide Fig. 9) | xÅ | (2πx/a) | yÅ | (2πy/b)° | zÅ | (2πz/c)° |
|---|---|---|---|---|---|---|
| A (CH) | −2.125 | −48.3 | −1.634 | −147.0 | −3.111 | −141 1 |
| B (CH) | −0.836 | −19.0 | −1.059 | − 95.8 | −2.702 | −122.8 |
| C (C) | −0.418 | − 9 5 | −0.536 | − 48.5 | −1 377 | − 62.6 |
| D (C) | 0.981 | 22.3 | 0.092 | 8.3 | −0.920 | − 41 8 |
| E (C) | 1.355 | 30.8 | 0.630 | 57.0 | 0.519 | 23.6 |
| F (CH) | 2.644 | 60.1 | 1.214 | 109 5 | 0.955 | 43.4 |
| G (CH) | 3.049 | 69.3 | 1 730 | 156.5 | 2.275 | 103.4 |
| H (O) | 1 729 | 39.3 | 0.155 | 14.0 | −1.650 | − 75 0 |

### Dimensions and orientation of the molecule

Diagramatic representation of the molecular dimensions together with interatomic distances and valency angles are given in Fig. 9. The distances are probably correct within 0.01 Å with a maximum possible error of ±0.02 Å. The valency angles are expected to be correct within 2°.

The final orientation of the molecules with reference to the crystallographic axes may be described as follows :—

Let us denote the axis passing through the centres of the three rings of anthraquinone as 'long axis' of the molecule and the axis joining the oxygen

atoms and the centre of the molecule as the 'cross axis' of the molecule. Then, the cross axis is very nearly parallel to the b-axis of the pseudo-orthorhombic cell and the position of the molecule is nearly attained by a tilt of the molecular plane about the b-axis so as to make an angle of about 27° with the (001) plane. Tilts about the other axes are of much smaller magnitudes If $\alpha$, $\beta$, $\gamma$ denote the angles made by the long axis of the molecule with the $a$, $b$, $c$ axes respectively and $\alpha'$, $\beta'$, $\gamma'$ be the corresponding angles made by the cross axis of the molecule, then these angles as worked out from the structure obtained are :—

$$a = 27°.4 \qquad\qquad\qquad a' = 88°.5$$
$$\beta = 91°.2 \qquad\qquad\qquad \beta' = 3°.8$$
$$\gamma = 62°.9 \qquad\qquad\qquad \gamma' = 86°.4$$
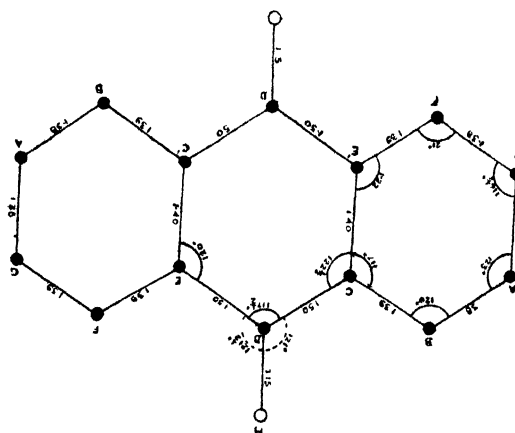


FIG. 9

Dimensions of anthraquinone molecule

## Molecular dimensions

| Interatomic distances in A U. | | | Valency angles. |
|---|---|---|---|
| Carbon-Carbon : | AB = 1 38<br>F'G' = 1.38<br>AG' = 1.385 | CH–CH<br>(Aromatic) | <ABC = 120°<br><BCE' = 117°<br>CE'F = 122° |
| | BC = 1.39<br>E'F' = 1.39 | C–CH | <E,F'G' = 121°<br><F'G'A = 116½° |
| | CE' = 1.395 | C—G | <G'AB = 123 |
| | CD = 1 50<br>DE = 1.50 | C–C<br>(" single bond ") | <E'CD = 122½°<br><CDE = 117½° |
| Carbon-Oxygen : | DH = 1.15 | C–O | <DEC' = 120°<br><CDH = 121°<br><EDH = 121½° |

*Arrangement of molecules in the crystal and molecular distances*

The dominant feature found in the anthraquinone structure is the grouping of molecules in a zig-zag way in space with the molecular planes in the alternate layers being inclined to one another at an angle of 54°. Molecular planes are inclined at an angle of 27° to the (001) plane. The zig-zag arrangement is best seen by projecting the structure on (010) plane as shown in Fig. 10. The molecules are, however, remarkably well resolved in the
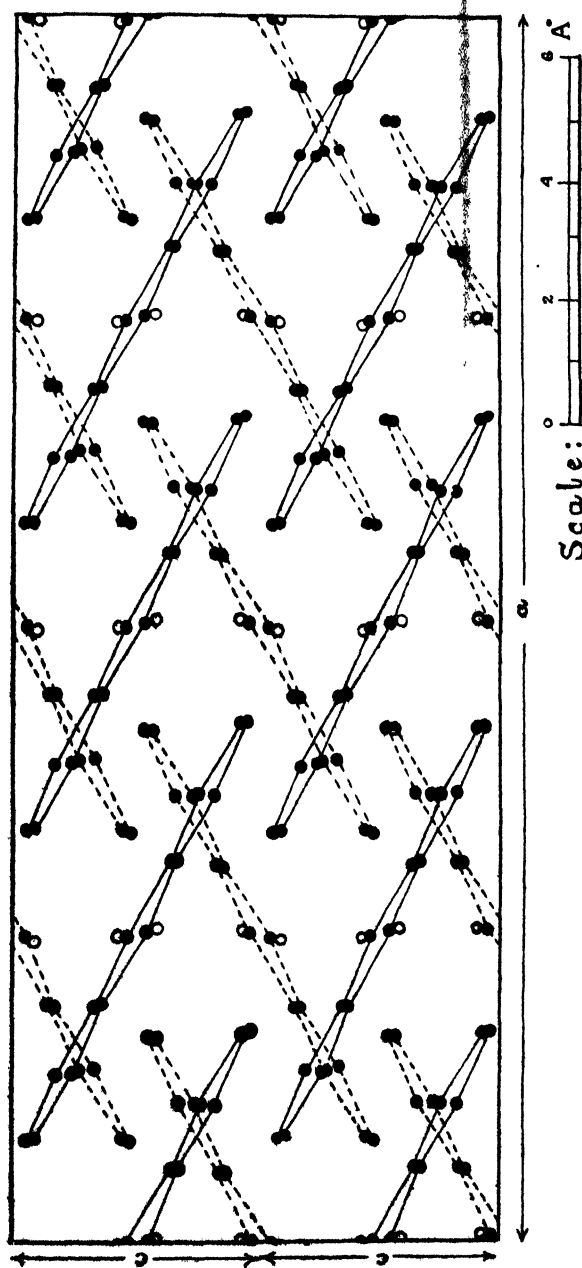


Fig. 10

Projection along old *b*-axis showing 8 molecules. The plane of each molecule is nearly perpendicular to the plane of projection.

projection along the symmetry axis (*i.e.*, old *c*-axis). Such a projection on a smaller scale showing the relations of a group of ₃2 molecules is shown in Fig. 11. To visualise how the molecules are arranged in space from the diagram (Fig. 11), it is to be imagined that the dotted molecules have their centres in planes ½*c* above and below those of the molecules shown with



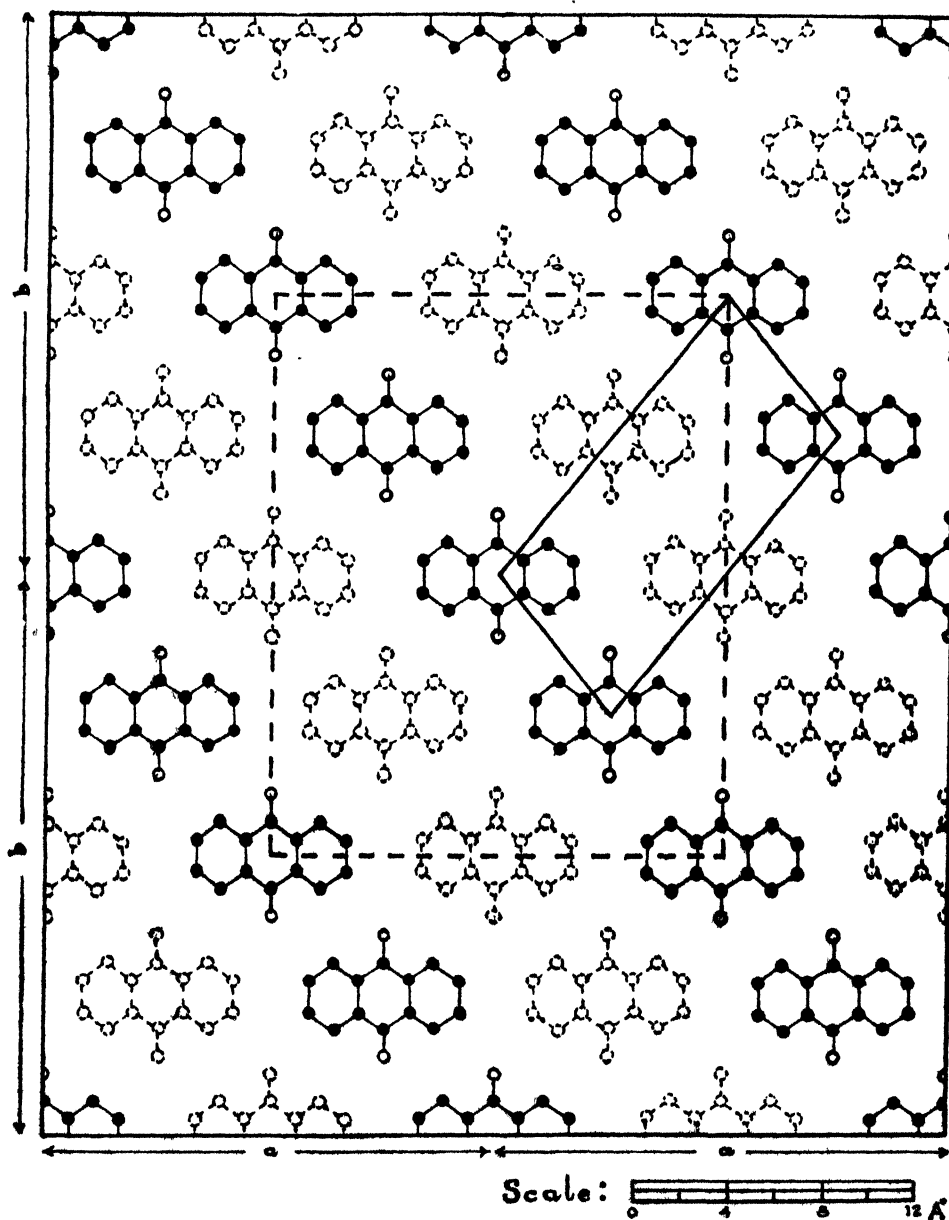FIG. 11

Projection along old *c*-axis showing the relation of a group of 32 molecules. The dotted molecules have their centres in planes *c*/2 above and below those of the molecules shown with black atoms,

shaded atoms. All the molecules are tilted from *ab*-plane (plane of the paper) by 27° about the *b*-axial direction passing through the centres of the molecule, the tilt of the dotted and shaded molecules being in opposite directions.

The nearest molecular approach occur between two molecules where one is derived from the other by the fundamental translation along *c*-axis ($c = 3.98$ Å). The perpendicular distance between the planes of these two molecules is approximately $3.98 \cos 27° = 3.54$ Å, which is, therefore, the minimum distance of approach between any two molecules. If Ā, B̄, C̄ etc. are atoms of the molecule derived by fundamental translation along *c*-axis of the molecule comprised of A, B, C , .. atoms (*vide* Fig. 9), the minimum intermolecular distance between carbon atoms occur between Ā and B ; B̄ and C ; C̄ and D and so on. Such distances when worked out range between 3.6 and 3.7 Å. In benzoquinone, corresponding observed distance is 3.45 Å, while in rescorcinol (Robertson, 1936), it is 3.6 Å. Minimum oxygen-oxygen inter-molecular distance in anthraquinone is the same as the fundamental translation of 3.98 Å. In benzoquinone, corresponding observed distance is 3.62 Å. The minimum intermolecular distance obtained in anthraquinone thus agree well with the usual order of such distances observed in other compounds.

*Peak values of electron density and electron counts*

The observed peak values of electron density for the different atoms in the *c*-axis projection where the atoms are remarkably well resolved are given in Table VI. The values are in general somewhat higher as compared to those observed in anthracene and benzoquinone. The values observed for the carbon atoms in the present case are between 7.5 to 9 electrons per square A.U. (6-7 observed in other structures). The peak values for the carbon atoms are found to gradually fall off as we pass outwards from the centre of the molecule, although one would ordinarily expect higher values for the outer CH groups as compared to the carbon atoms of the inner ring. A slight broadening of the end atoms is also observed. It is interesting to note that such falling off in the peak values of electron density as we pass out from the centre of the molecule, combined with a slight broadening of the structure has also been observed in the case of anthracene and other allied compounds. In anthracene, peak values were found falling gradually from 7 to 5.5 electrons per square A.U. towards the end of the molecule.

In the *c*-axis projection in which each of the atoms is distinctly resolved, electron counting was carried out by the method first used by Bragg (1929). Boundary lines were drawn round each of the atoms comprising half of the molecule as shown in Fig. 12. The appropriate electron densities $\rho(x, y)$ at intervals of $a/96$, $b/96$ were then summed up with appropriate weightage to fractional square near the boundary lines and number of electrons for each of the atoms calculated from the relation $N = \Sigma \rho(x, y) \times ab/96^2$. Results so obtained are given in Table VI. Electron
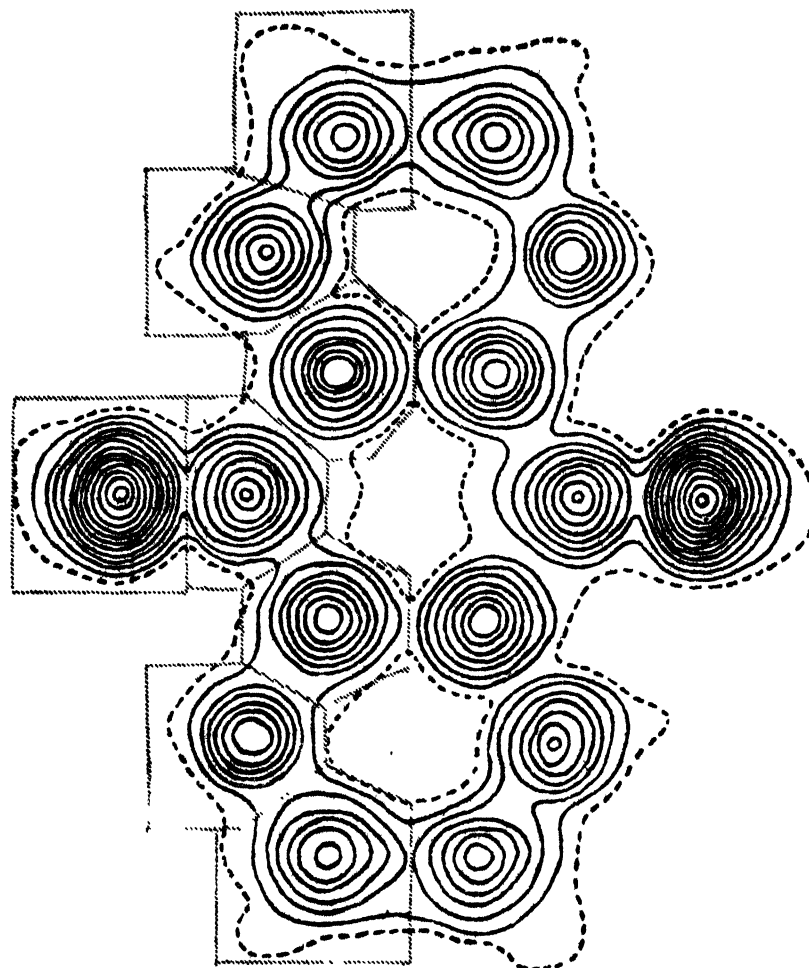
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FIG. 12

Electron count in anthraquinone molecule (projection along old c-axis)

TABLE VI

*Peak values of electron density : electron counts*

|        | Atom    | Peak value per sq. A U | Number of electrons |
|--------|---------|------------------------|---------------------|
| Carbon : | A CH₂  | 7.5                    | 6.8                 |
|        | B (CH)  | 7.4                    | 5.6                 |
|        | C (C)   | 8 8                    | 5.9                 |
|        | D (C)   | 9 0                    | 6.0                 |
|        | E (C)   | 8 2                    | 5.9                 |
|        | F (CH)  | 8.1                    | 6.0                 |
|        | G (CH)  | 7.4                    | 6.4                 |
| Oxygen : | H (O)  | 13.0                   | 9.5                 |

count for the oxygen atom gives 9.5 electrons instead of 8 as required by the atomic number. This suggests that the oxygen atoms in anthraquinone have partial ionic character. The discrepancy may also be partly due to inaccuracy in the intensity measurements and to the omission of the still weaker reflections in the Fourier series.

## DISCUSSION OF RESULTS
### *Revision of space group*

It will be seen that a wrong assumption of space group for the anthraquinone crystal under the orthorhombic system apparently frustrated all earlier attempts to determine its correct structure. It has now been established beyond doubt that the crystal belongs to the monoclinic system. The space group is found to be $C_{2h}^5 P_1^2/a$. The fact that the crystal developes very few faces has also been partially responsible for the earlier confusion in the classification of the anthraquinone crystal. The revision of the crystal class and the determination of its correct space group fully account for all the observed points which appeared anomalous on the assumption of orthorhombic nature of the crystal. The arrangement of the molecules in the crystal finally obtained clearly explains its pseudo orthorhombic nature.

It is noteworthy that a few very feeble reflections have been observed in a highly over-exposed Weissenberg photograph which are actually forbidden spectra for the space group $C_{2h}^5 P_1^2/a$ and thus, in the strict sense of space group, anthraquinone has to be classed under the bisphenoidal class with its space group as $C_2^2$. But the contribution of these few exceedingly feeble reflections towards structure would be so infinitesimally negligible that it can lead to no deviation from the centro-symmetrical structure of the molecule. The space group $C_{2h}^5 P_1^2/a$ has therefore, been assigned to the crystal.

### *Molecular dimensions and comparison with those of anthracene and benzoquinone*

The anthraquinone molecule has been found to be approximately planar. Though none of the three benzene rings in anthraquinone molecule is found to be perfectly regular hexagon, the two outer rings are very nearly regular with carbon to carbon distances varying between 1.38 Å and 1.40 Å. Thus each of these distances lies within the limits 1.39 Å ± .01. Corresponding distances found in anthracene (Robertson, 1933) is 1.41 Å, while in resorcinol (Robertson, 1936) it is 1.39 Å. The valency angles observed in the outer rings are between 117° and 123°. It is, however, difficult to say whether this deviation from 120° for these angles is genuine or only due to experimental error. The outer rings may, therefore, be considered to be regular plane hexagons, within the limits of experimental error, like those of the anthracene molecule. The central ring is, however, definitely distorted like benzoquinone molecule.

The "single" bond carbon to carbon distances in the central ring of anthra-quinone molecule are found to be approximately 1.50 Å which is identically the same value as observed in benzoquinone. One striking difference between the two structures is, however, noticed in the valency angles between the single bonds. In benzoquinone, the angle has the tetrahedral value of $109°\frac{1}{2}$, while in anthraquinone it is found to be 117°. The angle between the single and double bonds was found to be 125° in benzoquinone, but the double bond being absent in anthraquinone molecule, the corresponding valency angle in anthraquinone molecule occurs between a single and a conjugate bond as in the case of hexamethylbenzene (Lonsdale, 1929, or dibenzyl (Robertson, 1934) where these angles are approximately 120°. As would be expected in analogy with the measurements for hexamethylbenzene and dibenzyl, the valency angles between the single and the conjugated bonds of the central ring of the anthraquinone molecule are actually found to be 120°-122°. These angles thus being smaller than corresponding value of 125° observed in benzoquinone, the valency angle between the single bonds in anthraquinone must be proportionately greater than the benzoquinone value of $109°\frac{1}{2}$. This explains the observed value of 117° between the single bonds found in anthraquinone.

The carbon to oxygen distance in anthraquinone is found to be 1.15 Å which is almost the same as that observed in benzoquinone, namely, 1.14 Å. The band spectrum and infra-red absorption spectrum analyses of carbon dioxide vapour give the carbon to oxygen distance as 1.15 Å and 1.16 Å, respectively. In benzoquinone, the carbon to oxygen distance could not be measured directly because the carbon atom to which the oxygen is directly attached remained obscured in all the projections and it also became difficult to locate accurately the position of the centre of the oxygen atom as it appeared slightly elongated in the projection. In anthraquinone, however, both the carbon and oxygen atoms are very well resolved in the projection along the symmetry axis and centres of these atoms could be accurately located. Although a higher value of 1.25 Å has been found for the carbon to oxygen distance in urea (Wyckoff and Corey, 1934), the distance observed in anthraquinone supports the benzoquinone value and those observed in the case of carbon dioxide. The ketonic oxygen in anthraquinone is also thus seen to be rather similar to the oxygen in carbon dioxide.

### Chemical formula and the nature of the valency bonds

The alternative structural formula of anthraquinone are given below :—

The outer rings being found to be regular hexagons instead of alternate single and double bond distances, the formula (1) for anthraquinone does not correctly represent the molecule. Formula (2) based on the "centric" formula with unlinked bonds fully supports the observed structure of anthra-quinone molecule.

(1)                (2)
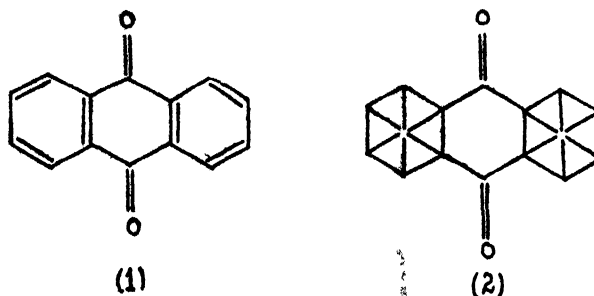
The stability and characteristic aromatic properties of substances have been attributed to a resonance between the different stable valance-bond structures which are termed 'canonical' structures of Pauling analogous to the resonance of benzene between two Kekule structures *viz.*



For anthraquinone, the following four stable valence-bond structures can be formulated :—
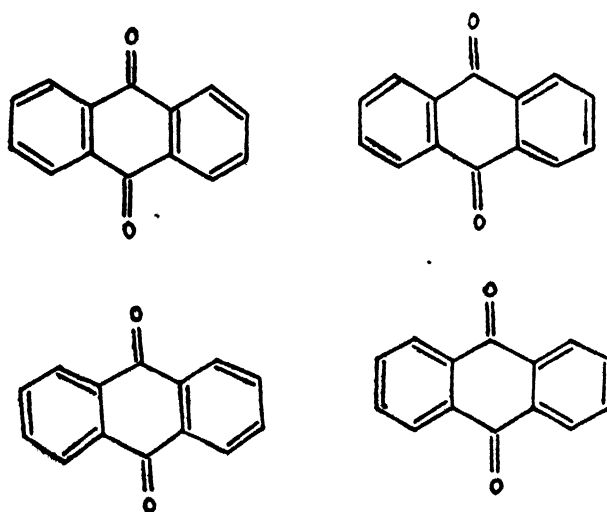


It will be seen that each of the bonds in the outer rings occurs as double bond in two of the above structures and as single bonds in the remaining two structures. That is, each of these may be considered to have 50% double bond character and in accordance with Pauling's curve (1935) such bond

corresponds to an interatomic distance of 1.39 Å. The observed distance agrees well with the above consideration.

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