THE CRYSTAL STRUCTURE OF METHYL SUBSTITUTED 1:2 - BENZANTHRAQUINONES

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THE CRYSTAL STRUCTURE OF

METHYL SUBSTITUTED 1:2-BENZANTHRAQUINONES

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by

ROBERT PATTON FERRIER

DECLARATION

I hereby declare that the following thesis is my own composition, that the work of which it is a record has been carried out by me, and that it has not previously been presented for a higher degree.

UNIVERSITY AND RESEARCH TRAINING

I entered Queen's College, Dundee in October, 1952, and in June 1955, gained the ordinary B.Sc. degree in Physics and Chemistry. I then read for honours in Physics, being awarded First Class Honours in Physics in June 1956. I received a Sir James Caird Travelling Scholarship and have completed three years research under the supervision of Dr. J. Iball, during which time the work contained in this thesis was performed.

CERTIFICATE

I certify that ROBERT PATTON FERRIER has spent eleven terms at research work under my supervision, and that he has fulfilled the conditions of Ordinance No. 16 of the University of St. Andrews, so that he is qualified to submit the following thesis in application for the degree of Ph.D.

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INTRODUCTION.

The subject of this thesis is the determination of the crystal and molecular structure of three organic compounds. Two of these compounds, 5-methyl 1:2-benzanthraquinone and 2'-methyl 1:2-benzanthraquinone, are of interest because of their relationship to the corresponding methyl substituted 1:2-benzanthracenes; 5-methyl 1:2-benzanthracene is carcinogenic, whereas the 2'-methyl derivitive has no biological activity (Barry et. al., 1935). Also if the structures can be determined accurately, then useful information will be obtained about the interatomic distances in the anthraquinone type of structure. The third compound investigated was the cis-isomer of 9:10-dimethoxy-carbonyl 9:10-dihydroanthracene. The interest in this compound is mainly steriochemical, the parent compound 9:10-dihydroanthracene being folded about the 9:10 axis (Ferrier and Iball, 1954).

The first stage in the determination of a crystal structure is to derive the unit cell, which is the repeat unit of the crystal, and to find the relationships of the molecules within that unit. When an x-ray beam is incident upon a crystal, each set of parallel planes will give a single diffracted wave which can be recorded photographically as a spot. From an examination of the positions of these spots it is possible to determine the dimensions of the unit cell. If the density of the crystal and the molecular weight of the compound are known, then the number (n) of molecules in the unit cell can be determined from the equation.

$$n = N\rho V/M$$

where M is the molecular weight of the compound,

V is the volume of the unit cell,

N is Avogadro's number,

and ρ is the density of the crystal.

Furthermore by observing any systematic absences in groups of reflections it is often possible to derive the space-group uniquely or at least to limit the space-group to two, or in a few cases three, possibilities. To distinguish between alternative space-groups other information must be used.

The waves diffracted from a set of crystal planes have associated with them an amplitude F(hkl), called the structure amplitude, and a phase. The structure amplitude of a set of planes can be determined by measuring the reflected intensity which, after correction for certain 'geometric' factors, gives the square of the structure amplitude (Chap.III, sect.(a)).

The major problem in x-ray crystallographic structure work is one of phase determination. The methods used to derive the phase of a given structure factor fall into two main groups - direct and indirect methods.

(a) <u>Direct Methods</u>.

Only one direct method was used in this work, that of Harker-Kasper inequalities (Harker and Kasper, 1948). This method will be discussed in Chapter IV, section (b,I).

(b) Trial and Error Methods.

The basis of the method of trial and error is to use any information available to postulate an atomic arrangement which conforms with the space-group symmetry and to calculate the structure factors (structure amplitudes) it would give for certain reflections. From the agreement between the observed and calculated structure factors an estimate of the correctness of the proposed structure can be obtained. One method of doing this is to calculate the reliability index, R, which is defined by,

$$R = \Sigma \big| |F_o| - |F_c| \big| / \Sigma |F_o|$$

where Σ extends over all the observed structure factors $F_o(hkl)$. The value of R should decrease as the structure approaches the correct one. The methods of weighted reciprocal lattices, optical transforms and Patterson syntheses are the basis for a more exact and speedier approach to the trial and error method and will be discussed in detail in later chapters.

The distribution of electron density within the unit cell is periodic and can be represented therefore by a Fourier series,

$$\rho(x,y,z) = \frac{1}{V}\sum\sum_{-\infty}^{\infty}\sum F_o(hkl) \text{ exp. } 2\pi i.(hx/a + ky/b + lz/c)$$

where V is the volume of the unit cell.

Hence once an approximate structure has been derived, the phases of the calculated structure factors, together with the observed structure factors, can be used to calculate a Fourier synthesis. The labour involved in computing a full three-dimensional Fourier series is prohibitive unless an electronic computer is available and the technique generally used is to compute two-dimensional Fourier projections. The positions of the maxima in the electron density plot are taken as the atomic positions and the co-ordinates of the atoms can thus be derived. These new co-ordinates can be used to recalculate the structure factors and refine the phases. Hence by successive Fourier syntheses, involving an increasing number of structure factors, the co-ordinates can be refined i.e. at each stage of the refinement a structure is obtained which approximates more and more closely to the correct structure. The other two methods which were used in this work to refine atomic co-ordinates were,

(1) successive ($F_o - F_c$) Fourier syntheses (Cochran, 1951),

and (2) the method of least squares (Hughes, 1941).

The two methods mentioned above will be discussed in detail in Chapter III sections (c) and (d).

CHAPTER I.

APPARATUS AND TECHNIQUES.

(a) X-ray Generating Units.

Two Phillips x-ray generating units were used in this research. One of them was of the constant output type in which the output voltage and current are stabilised. This unit was used principally in the determination of accurate x-ray intensities using a Geiger counter spectrometer.

(b) Cameras.

The three types of x-ray cameras used were,

(1) a Unicam single crystal x-ray goniometer for rotation and oscillation photographs,

(2) a Buerger Precession camera (Buerger, 1944),

and (3) a Leeds-Cox Weissenberg goniometer for moving film photographs.

The Leeds-Cox camera was modified to give a uni-directional integrated spot (Stanley, 1955). In the later stages of the research the manually operated integrating device was made fully automatic (Iball, 1959).

(c) Structure Factor Calculating Machines.

In the initial stages of a crystal structure determination, a structure factor machine of the type described by Bragg (Bragg, 1952) was used. The machine operates on the principle of moments and on it the structure factor is weighed. The accuracy of the machine, however, is limited. When the structure factors were required more accurately, they were calculated on a desk electric Facit calculating machine.

(d) The Optical Diffractometer.

The principle of the optical diffractometer was first suggested by Bragg (Bragg, 1944) and developed by Lipson and Taylor (Lipson and Taylor, 1951).

The molecular model to be investigated is represented by a number of holes punched in an opaque mask using the Pantograph punch. The Fraunhofer diffraction pattern, in parallel monochromatic light, is observed in the focal plane of the objective lens, where it can be studied with the aid of a microscope or photographically.

The technique generally used was to punch, not just one molecule, but the contents of four unit cells. The molecules must have exactly the same relationships to one another as they do in the real crystal. The resulting transform can then be compared directly with the weighted reciprocal lattice (See Chap.III, sect.(b)).

(e) The Measurement of X-ray Intensities.

Three methods of estimating the intensity of x-rays reflected from a crystal plane were used in the investigation.

(i) Visual Estimation of Intensities.

The reflections from a crystal zone were recorded on x-ray film using the Leeds-Cox Weissenberg goniometer. The multiple film technique developed by Robertson (Robertson, 1943) was used. Three Ilford "Industrial G." x-ray films, separated by one layer of black paper, were packed into the camera. The interfilm absorption ratio was measured for each batch of film using the Geiger counter spectrometer (Chap.I, sect.(e,iii)). The intensities were correlated by means of this ratio. It was found that, in general, the range of intensities from a particular zone could be covered by two exposures, one long and one short. The relative intensities of the reflections were estimated by visual comparison with a series of spots on a multiple exposure strip, prepared by taking a set of carefully timed oscillation photographs side by side on an Ilford "Industrial G." x-ray film.

(ii) Measurement of Intensities Using the Double-beam Recording Microdensitometer.

This instrument, manufactured by Joyce, Loebl and Co. Ltd., and based on the design developed by Walker (Walker, 1955) was only available in the later stages of the work. The principle of operation is based on a double-beam light system, in which light from a single source is split into two beams which are switched alternately to a single photomultiplying cell. One beam passes through the photographically recorded spot from a crystal plane and the other through a "grey" optical density wedge. If the two beams have different intensities, a difference signal is produced by the photomultiplier, which, after amplification, causes a servo motor to move the optical density wedge so as to reduce the intensity difference to zero. In this way a continuously balancing system is obtained and as the spot is scanned a record of the density response is obtained and recorded on graph paper by a pen, the movement of which is linked directly to that of the optical wedge.

The optical density wedges supplied with the instrument were found to be non-linear, the departure from linearity being most marked at the ends of the wedges. For this reason it was decided to calibrate the displacement of the wedges against x-ray intensity. Only the middle portion of a wedge was used i.e. a length of approximately 18 cm. The calibration was carried out using a series of spots of known intensity prepared on x-ray film by a series of carefully timed exposures, using the constant output x-ray generator. The instrument was set to record the intensity of the unexposed film at 3 cm. from the bottom of the wedge. This was taken as the reference point in the correlation of wedge displacement and x-ray intensity, and graphs were drawn calibrating the wedges.

In an actual measurement of the photographically recorded x-ray intensities from a crystal zone, it was found desirable to use a

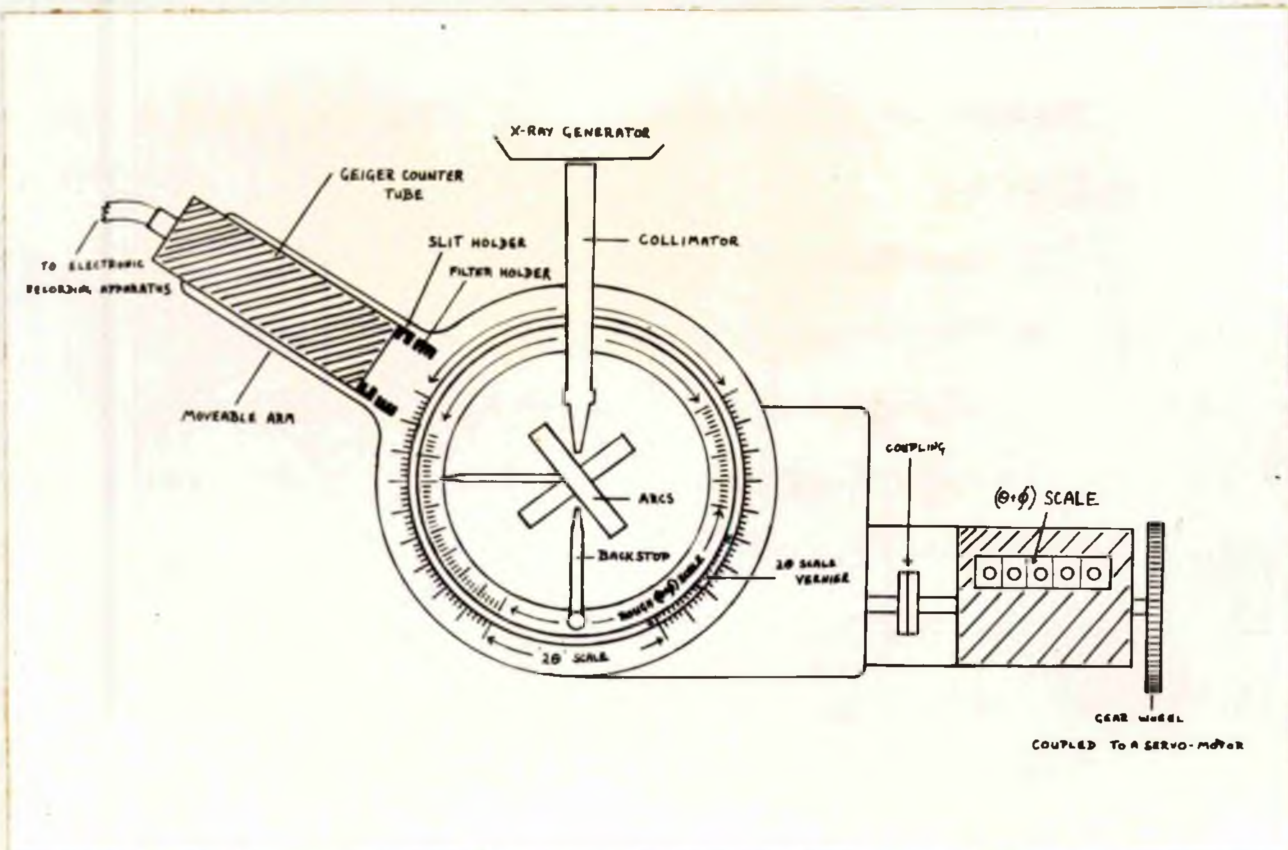

Fig. 1.1. The Geiger counter spectrometer.

linearly integrated spot and to measure only the intensity of the uniform middle portion of the spot. The values of the intensity at the peak of the reflection and the background intensity are read from the graph and the difference between them is the value of the actual peak intensity.

(iii) The Measurement of X-ray Intensities Using the Geiger Counter Spectrometer.

The measurement of photographically recorded x-ray intensities, by visual comparison or by recording microdensitometer, is subject to fairly large errors, especially in the case of visual estimation. To improve the accuracy of intensity determination, the ideal method would be to detect directly the x-ray quanta reflected from a crystal by proportional or scintillation counters. Suitable types of these counters were unavailable at the time of the investigation and a Geiger counter was used. The Geiger counter has one disadvantage in that the rate of counting is limited by the comparitively long dead-time of the counter tube - between 200 and 400 microseconds.

(a) Apparatus.

The Geiger counter spectrometer used was designed by Dr. Iball and a diagram of the instrument is shown in Figs. I,I.*

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* The figures and tables in this thesis will be given two numbers. The first number refers to the appropriate chapter and the second number to the sequence of diagrams or tables within that chapter.

The principle is one of rotating crystal and stationary detector. The crystal rotation was obtained by a coupling between the goniometer head and a servo motor, in which the speed could be varied in fixed ratios. The ratio between the speed of the motor and the rotation speed of the crystal was reduced by a gear-train located inside the body of the spectrometer. The reduction factor was 3600:1. The Geiger counter tube is fixed to a movable arm and aligned parallel to the incident x-ray beam. The effective aperture of the Geiger counter tube is altered by various slits cut in brass plates and inserted in a holder (see Fig.1,1). The holder also has slots cut in it to take filters of either nickel foil of uniform thickness or pieces of x-ray Ilford "Industrial G" type film.

The geometry of x-ray reflection is such that, if θ is the Bragg angle for a particular plane and ϕ is the angle which that plane makes with a reference plane in the crystal - generally taken as either (100) or (010) or (001) plane - then the reflection position of the plane with respect to $\phi = 0$, is given by the angle $(\theta + \phi)$ and the x-rays reflected from the plane are detected at an angle 2θ with respect to the undeflected x-ray beam. The scales recording $(\theta + \phi)$ and 2θ are shown in Fig.1,1. The $(\theta + \phi)$ counter can be read to $\pm 0.002^\circ$ and the 2θ vernier scale can be read to $\pm 0.03^\circ$. A rough $(\theta + \phi)$ scale is also available and is used in the setting of the crystals.

The pulses from the Geiger counter tube were recorded using standard electronic equipment. The equipment includes a recording ratemeter which was used to record the profiles of the crystal reflections. A pulse counter controlled by an automatic timer was also used. This enables either the number of counts in a given time or the time for a specific number of counts to be determined.

If the results obtained from a determination of a set of intensities are to be reliable, the x-ray generating unit must be of the constant output type. Nickel filtered copper radiation was used throughout the intensity determinations.

(b) Preliminary Setting Technique.

In the determination of the intensities of the reflections from a crystal zone by Geiger counter measurements, it was found extremely useful to have a "rough" set of intensities previously measured by visual estimation. From unit cell measurements the values of $(\theta + \phi)$ and 2θ were determined for each reflection in the zone (the value of $\phi = 0^{\circ}$ is assigned to an axial set of reflections) and were then set out, in table form, in increasing order of $(\theta + \phi)$.

The crystal was now set to rotate about the required crystal axis using the photographic technique and then transferred to the Geiger counter spectrometer. Before commencing intensity measurements, it was first ascertained that the reflected beam from any reflection, the intensity of which was to be measured, passed through the centre of the slit placed in front of the Geiger counter tube. The setting of the crystal was controlled by two adjustable arcs at right angles to one

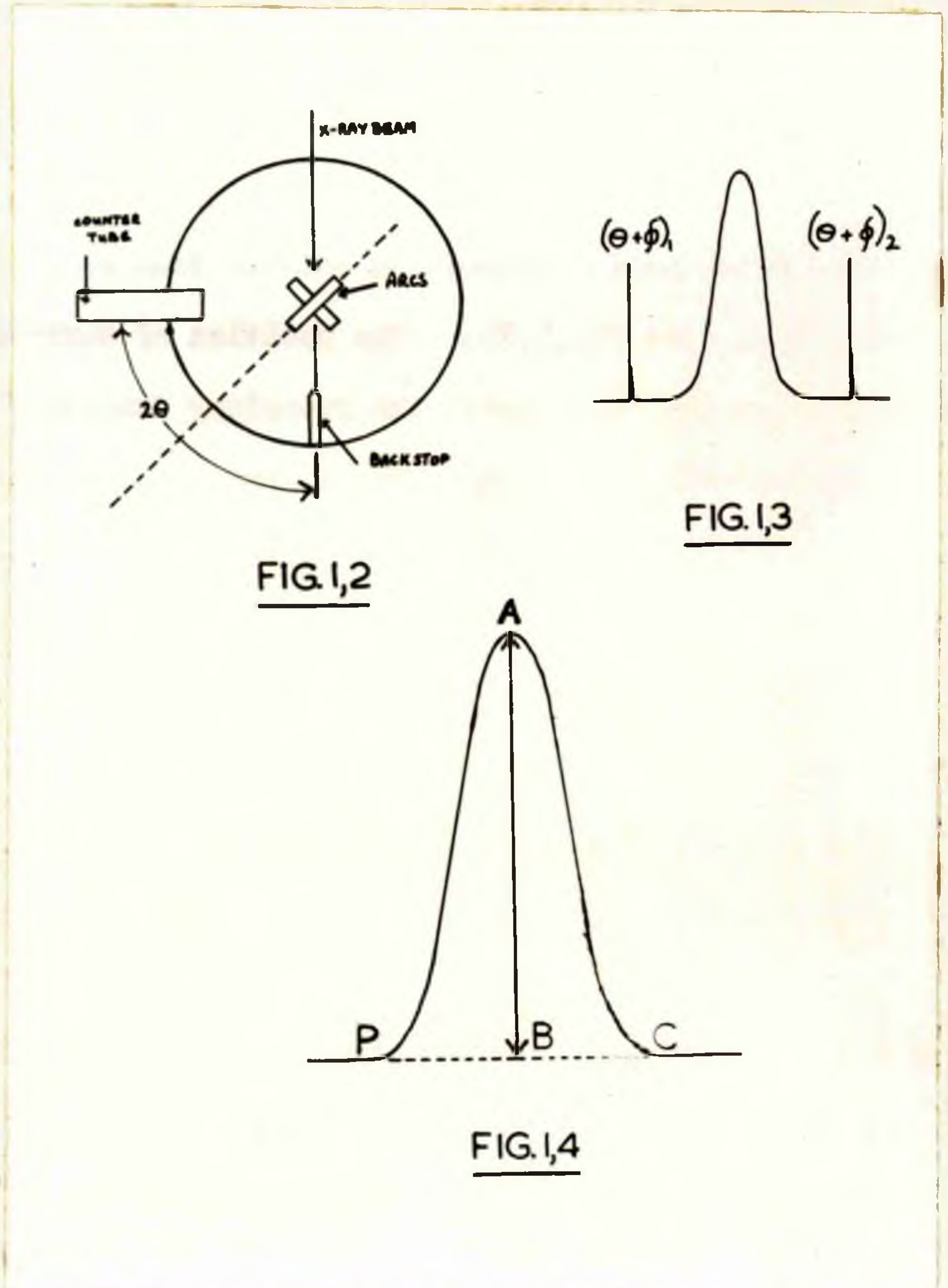

Fig. 1.2. The experimental technique used to set a crystal on the Geiger counter spectrometer.

Fig. 1.3. The determination of the accurate reflecting position using the ($\theta + \phi$) scale.

Fig. 1.4. Theoretical reflection profile.

another and each arc was set individually in the following way. A reflection was selected which had a 2θ value of approximately 90° and was such that, in the reflecting position, one arc as near as possible bisected the angle between the counter tube and the undeflected x-ray beam (see Fig.1,2). The position of maximum intensity of the reflection was found using the recording ratemeter and the crystal was stopped in that position. The appropriate arc was then adjusted to allow the reflected beam to pass through the middle of the slit. The whole process was then repeated for the other arc.

The $(\theta + \phi)$ scale was set so that $\phi = 0^\circ$ for the reference reflections and the technique used was as follows. The Geiger counter was set to record an axial reflection of reasonable intensity. The crystal was slowly rotated through the reflecting position and the value on the $(\theta + \phi)$ scale for maximum intensity was noted. To obtain a more accurate value of the reflecting position, the crystal was once more rotated slowly with uniform velocity through the reflecting position and the profile recorded on the recording ratemeter. When the crystal was about 1° from the peak position, an extra electric impulse was applied to the recorder and a reference line was drawn on the paper. The peak was scanned and another reference line made on the paper as shown in Fig. 1,3. From the known values of $(\theta + \phi)$ at which the reference lines were made, an accurate estimate of the profile peak was made. The same axial reflection will occur at an angle $- 2\theta$ from the first reflecting position and the Geiger counter was set at $- 2\theta$

to record this reflection. The value of $(\theta + \phi)$ at which the reflection occurs was recorded with the crystal rotating in the same direction as in the first case, to avoid any error due to instrument back-lash. Thus two values of $(\theta + \phi)$ were obtained for a reference reflection on either side of the true $(\theta + \phi)$ scale zero position. The $(\theta + \phi)$ counter was then set at zero for the mean value of $(\theta + \phi)$ obtained.

(c) Intensity Measurements.

If the profile of a reflection is considered (Fig.1,4), the intensity can be measured in two ways. Either the peak height AB is determined or more accurately the area PACP under the profile curve is found. The latter "integrated" intensity was the value measured on the Geiger counter spectrometer.

In an actual measurement of the intensities from a crystal zone, the lowest intensity which was to be recorded was decided on the basis of a previous visual estimation of the intensities. The output of the x-ray generator was adjusted to give, in the case of the weakest reflection, a peak height above the background of approximately $1/10^{th.}$ full scale deflection on the lowest scale of the recording ratemeter. Once the output of the x-ray generator was fixed, it remained unaltered throughout a determination.

The speed at which each reflection is scanned must be determined for each crystal from the average profile of the reflections. It was generally of the order of 2° to 3° in two minutes. For example, if the rotation speed was fixed at 2.6° in two minutes, each plane was first scanned through the reflecting position and the profile recorded. If the profile was normal, the crystal was set back to 1.3° from the peak reflecting position and a count was taken of the background intensity over a period of one minute. The crystal was then rotated at the fixed speed through the reflecting position from $(\overline{\theta + \phi} - 1.3)^{\circ}$ to $(\overline{\theta + \phi} + 1.3)^{\circ}$ and the count over this two minute period was recorded. Another background count was then taken at $(\overline{\theta + \phi} + 1.3)^{\circ}$ for one minute. The sum of the background counts gave an estimate of the background intensity during the period of scan of the reflection. After correction for lost counts due to the counter dead-time, the difference between the peak and background counts gave the true integrated intensity.

The positions at which the background counts were made, were judged for each reflection individually on the basis of the reflection profile.

The integrated intensity of each reflection was estimated at $(\theta + \phi)^{\circ}$ and also at $(180 + \overline{\theta + \phi})^{\circ}$.

It was found inadvisable to count at rates exceeding a maximum value of 400 counts per second, because the percentage correction for lost counts became too great above that value. The rate of count for the stronger reflections was reduced below the maximum value by cutting down the intensity of the reflected beam by filters of either nickel foil or x-ray film.

At intervals throughout the determination of the intensities from a crystal zone, the "natural" background was measured with the window of the x-ray set closed. The measurements were made over periods of 10 minutes and the average number of counts per second was estimated.

(d) Determination of Filter Factors and the Correction for Lost Counts in Integrated Intensities.

The crystal was set at the peak reflecting position for a suitable reflection. The number of counts over periods of two minutes, with and without a filter, was recorded. This was repeated several times to give a sufficient number of counts for a reasonable statistical accuracy. The individual values of counts per second, with and without the filter, were corrected for lost counts and the natural background was subtracted.

When the counter is receiving x-rays at a constant rate, the equation for the correction due to lost counts can be written in the form (Lewis, 1948),

$$N_0 = N_1/(1 - aN_1) \qquad (1).$$

where N_0 is the corrected number of counts per second,

N_1 is the recorded number of counts per second,

and a is the resolving time of the counter tube.

Now in the filter factor determination, if

N_1 is the number of counts per second without the filter,

N_2 is the number of counts per second with the filter,

$\overline{N_N}$ is the average number of counts per second due to the natural background

and F is the absorption factor of the filter,

then

$$\left[N_1/(1 - aN_1) - \overline{N_N}\right] = F\left[N_2/(1 - aN_2) - \overline{N_N}\right] \quad (2)$$

Equation (2) is solved for each pair N_1, N_2 and the mean value of F determined.

In the determination of the integrated intensity of a reflection, the rate of counting is observed to vary over the range of $(\theta + \phi)$ scanned. The value of a in equation (1) is therefore not the resolving time of the counter and must be determined experimentally in the following way.

Five or six reflections were selected which had normal profiles and which gave peak intensities ranging from 150 to 400 counts per second. For each reflection the peak was scanned with and without a filter of known absorption factor and the number of counts in two minutes was recorded. This was repeated several times to give a reasonable number of counts. The range, speed and direction of scan was the same in each case.

Considering each reflection in turn, if

$\overline{N_1}$ is the average number of counts in two minutes without a filter,

$\overline{N_2}$ is the average number of counts in two minutes with a filter,

$\overline{N_N}$ is the average number of counts per second due to the natural background,

a_e is the correction factor for the integrated intensity,

and F is the absorption factor of the filter,

then

$$\left[\overline{N_1}/(1 - a_e\overline{N_1}) - 120\,\overline{N_N}\right] = F\left[\overline{N_2}/(1 - a_e\overline{N_2}) - 120\,\overline{N_N}\right] \quad (3)$$

Using equation (3) a_e was determined for each of the reflections used and a mean value was estimated.

(e) Relative Intensities.

In general the correction for lost counts in the background count was negligible and the relative integrated intensity of any reflection of the crystal zone can be written,

$$I = F\left\{\left[\overline{N_1}/(1 - a_e\overline{N_1}) - 120\,\overline{N_N}\right] - \left[\overline{N_B} - 120\,\overline{N_N}\right]\right\}$$

$$= F\left[\overline{N_1}/(1 - a_e\overline{N_1}) - \overline{N_B}\right] \quad (4)$$

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where $\overline{N_1}$ is the average number of counts in two minutes of the integrated peak,

$\overline{N_B}$ is the average number of counts in two minutes from the background,

and F is the absorption factor of the filter used.

(f) Discussion.

The process of measuring intensities on the Geiger counter spectrometer is long and tedious. The accuracy with which the weak intensities can be measured is relatively low, unless a great deal of time is spent repeating the measurements to give a sufficient number of counts for reasonable statistical accuracy. Hence in an actual measurement of the intensities from a crystal zone, the stronger intensities were obtained on the Geiger counter spectrometer and the weak intensities were estimated visually from equi-inclination photographs.

(g) Other Uses of the Geiger Counter Spectrometer.

Determination of Accurate Cell Dimensions -

The Geiger counter spectrometer enables the dimensions of the unit cell of a crystal to be measured accurately.

To measure axial spacings the value of the Bragg angle θ for a suitable axial reflection is measured by determining the angle 2θ between the reflecting positions at $(\phi + \theta)$ and $(\phi - \theta)$ (see section (e,1b) of this chapter). The axial spacing can then be calculated from the Bragg equation,

$$2d.\sin\theta = n\lambda.$$

To increase the accuracy of the determination, a reflection with as large a value of θ as possible should be used.

The angle between two crystal planes e.g. the (100) and the (010) can be determined in the following way. The $(\theta + \phi)$ scale is set so that $\phi = 0^\circ$ for the axial reflections (h00). The values of the reflecting positions $(\phi + \theta)$ and $(\phi - \theta)$ of an axial reflection (0k0) are then determined and from the known value θ for the reflection the value of ϕ, the angle between the planes (100) and (010) can be determined.

Measurement of Interfilm Absorption Ratios.

To enable the correlation of intensities in a visual estimation (section (e,1) of this chapter) the interfilm absorption ratios can be measured on the Geiger counter spectrometer. The absorption factor of a filter, consisting of a sample piece of Ilford "Industrial G" film and one layer of black paper, is measured using the technique described in paragraph (d) of this section.

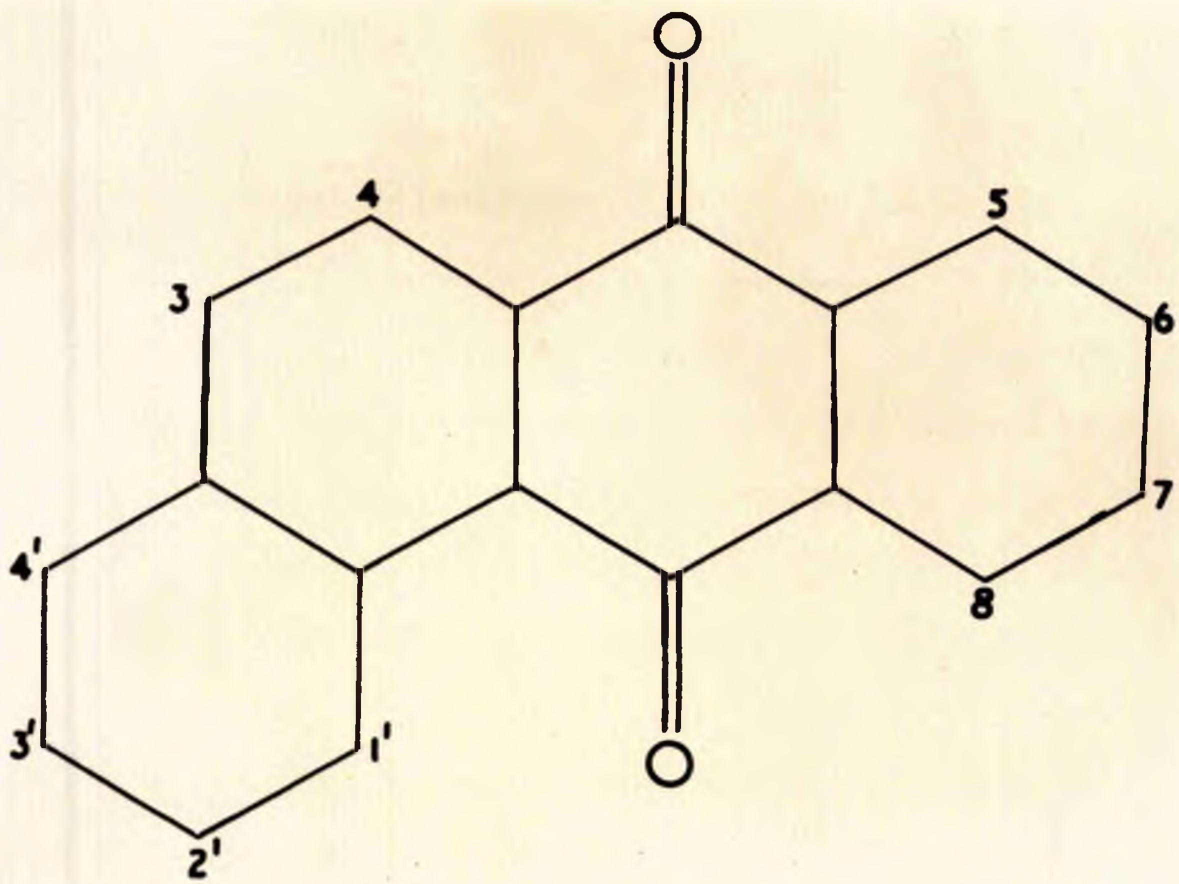


Fig. 2.1. The molecule of 1:2-benzanthraquinone, showing the numbering of the carbon atoms at which methyl substitution can take place.

CHAPTER II.

THE SPACE-GROUPS AND UNIT CELL DIMENSIONS OF THE METHYL SUBSTITUTED 1:2-BENZANTHRAQUINONES ($C_{19}O_2H_{12}$).

(a) Introduction.

The methyl substituted derivitives of 1:2-benzanthraquinone were prepared in London by J.W. Cook, Mrs. A.M. Robinson and F. Goulden (Cook, 1930, 1932, 1933; Cook, Robinson and Goulden, 1937). The standard nomenclature is as shown in Fig. 2,1. The preparation was undertaken with a view to correlating the oxidation - reduction potentials of the methyl substituted 1:2-benzanthraquinones and the biological activity of the corresponding methyl substituted 1:2-benz-anthracenes (Ihall, 1940).

On recrystallization many of the methyl substituted 1:2-benzanthraquinones gave crystals which were not satisfactory and great difficulty was experienced in obtaining single crystals which were free from multiple splitting.

In the determination of the space-groups and unit cell dimensions of the compounds, a suitable crystal was selected and this was set to rotate about one of the principal axes. Zero, first and second layer Weissenberg moving film photographs were then taken using the Leeds-Cox Weissenberg goniometer. The crystal was then transferred to the Buerger Precession camera and the other two main zones were photographed. It was found very helpful in setting the crystal on the Precession camera if the original axis of rotation was not too short. All photographs were taken using copper Kα radiation and measurements of the reflection positions were made using a Cambridge universal measuring instrument and the Buerger Precession camera measuring instrument. The densities of the crystals were determined by the method of centrifuge flotation and the medium used was an aqueous solution of cadmium boro-tungstate.

(b) 1:2-Benzanthraquinone.

This compound was recrystallised from ethyl acetate and dark-yellow plates were obtained. The crystals were found to be monoclinic and the cell dimensions were measured and are as follows:-

$\underline{a}$ = 10.96 ± 0.03 A.U.

$\underline{b}$ = 11.70 ± 0.03 A.U. $\beta = 96.8^\circ \pm 0.2^\circ$

$\underline{c}$ = 19.23 ± 0.06 A.U.

The cell edges $\underline{a}$ and $\underline{c}$ lie in the directions of the diagonals of the main face of the plate crystal.

Number of molecules in the unit cell	= 8
Volume of unit cell	= 2448.9 A.U.^{3}
Calculated density	= 1.400 g./cc.
Observed density (26.3°C.)	= 1.398 ± 0.004 g./cc.

The systematic absences observed were,

(hkl) absent when h+k is odd,

(hol) absent when l is odd.

The space-group is therefore C_c or $C2/c$. No distinction can be made between the alternative space-groups on the above evidence.

(c) <u>3-Methyl 1:2-Benzanthraquinone</u>.

This compound was investigated by Iball (Iball, 1938) and the results of his work are summarised below.

The crystals were obtained in the form of needles by recrystallisation from ethyl acetate. They were found to be monoclinic and showed the forms $\{011\}$ and $\{100\}$. The direction parallel to the length of the needles was chosen as the a - axis. The dimensions of the unit cell were measured and are as follows:-

a = 7.52 A.U.

b = 16.81 A.U. β = 118.9°

c = 11.63 A.U.

Number of molecules in the unit cell	= 4
Calculated density	= 1.403 g./cc.
Observed density	= 1.396 g./cc.

The systematic absences observed were,

(h0l) absent when h is odd,

(0k0) absent when k is odd.

The space-group is therefore $P2_1/a$.

(d) <u>4-Methyl 1:2-Benzanthraquinone</u>.

This compound was recrystallised from ethyl acetate. The crystals formed were light-brown in colour and needle shaped. The crystals were found to be monoclinic and the c - axis was chosen parallel to the needle axis. The cell dimensions were measured and are as follows:-

a = 11.80 ± 0.03 A.U.

b = 15.50 ± 0.04 A.U. β = 117.8° ± 0.2°

c = 3.99 ± 0.01 A.U.

Number of molecules in the unit cell	= 2
Volume of the unit cell	= 647.3 A.U.^{3}
Calculated density	= 1.397 g./cc.
Observed density (22.0°C)	= 1.400 ± 0.004 g./cc.

The only systematic absences observed were,

(oko) absent when k is odd.

The space-group is therefore $P2_1$ or $P2_1/m$. However, the space-group $P2_1/m$ requires 4 asymmetric units in the cell and the actual cell contains only two molecules which possess no centre of symmetry. Hence the space-group is $P2_1$.

(e) <u>5-Methyl 1:2-Benzanthraquinone</u>.

This compound was recrystallised from ethyl acetate and gave long straw-coloured needles with a well developed face - later identified as the (010) face - parallel to the needle axis. The cell dimensions were measured and are as follows:-

a = 14.13 ± 0.01 A.U.

b = 23.27 ± 0.02 A.U.

c = 3.94 ± 0.01 A.U.

The axial lengths **a** and **b** were obtained from measurements made on the Geiger counter spectrometer.

Number of molecules in the unit cell	= 4
Volume of unit cell	= 1295.5 $A.U.^3$
Calculated density	= 1.395 g./cc.
Observed density (24.5°C)	= 1.389 ± 0.004 g./cc.

The systematic absences observed were,

(hol) absent when h+l is odd,

(hko) absent when k is odd.

The space-group is therefore $P2_1nb$ or Pmnb. However Pmnb requires 8 asymmetric units per unit cell and the above cell contains only 4 molecules which have no centre of symmetry. Therefore the space-group is $P2_1nb$.

(f) 6-Methyl 1:2-Benzanthraquinone.

This compound was recrystallised from amyl acetate and straw-coloured needles were obtained. The crystals were found to be triclinic and the cell dimensions were measured and are as follows:-

a = 13.12 ± 0.03 A.U.	α = 103.0° ± 0.2°
b = 13.69 ± 0.03 A.U.	β = 94.8° ± 0.2°
c = 7.68 ± 0.02 A.U.	γ = 83.1° ± 0.2°
a^* = 0.1186 ± 0.0003 $A.U.^{-1}$	α^* = 77.4° ± 0.2°
b^* = 0.1162 ± 0.0003 $A.U.^{-1}$	β^* = 95.9° ± 0.2°
c^* = 0.2065 ± 0.0006 $A.U.^{-1}$	γ^* = 86.6° ± 0.2°

Number of molecules in the unit cell	= 4
Volume of the unit cell	= 1331.5 A.U.^{3}
Calculated density	= 1.358 g./cc.
Observed density (23.0°C)	= 1.359 ± 0.004 g./cc

The crystal is triclinic and hence the space-group may be either P1 or P$\bar{1}$. No deduction can be made between the alternative space-group on the basis of the evidence so far obtained.

(g) <u>7-Methyl 1:2-Benzanthraquinone</u>.

Many attempts were made, using different solvents, to obtain crystals of the above compound, which were large enough to enable measurements to be carried out. All efforts were unsuccessful and accordingly no observations were made on the space-group and unit cell dimensions.

(h) <u>8-Methyl 1:2-Benzanthraquinone</u>.

The crystals of this compound were obtained, on recrystallisation from ethyl acetate, in the form of straw-coloured needles. On preliminary examination under the polarising microscope the crystals appeared to be single crystals. However on x-ray examination it was found almost impossible to obtain a crystal which was free from multiple splitting. Individual fragments, which were apparently single crystals, were much too small and so the work was performed on a crystal which was only slightly split.

The crystals were found to be monoclinic and the c - axis was chosen parallel to the needle axis. The cell dimensions were measured and are as follows:-

$\underline{a}$ = 10.37 ± 0.03 A.U.

$\underline{b}$ = 16.91 ± 0.04 A.U. β = 100.5° ± 0.2°

$\underline{c}$ = 7.57 ± 0.03 A.U.

Number of molecules in the unit cell = 4

Volume of the unit cell = 1305.2 A.U.^{3}

Calculated density = 1.393 g./cc.

Observed density (22.0°C) = 1.388 ± 0.004 g./cc.

The systematic absences observed were,

(h0l) absent when l is odd,

(0k0) absent when k is odd.

Therefore the space-group is unequivocally $P2_1/\underline{c}$.

(i) <u>1'-Methyl 1:2-Benzanthraquinone.</u>

This compound was recrystallised from ethyl acetate and yellow needles were obtained. The crystals were found to be monoclinic with the needle axis as the unique axis $\underline{b}$. The crystals were found to have quite well developed (100) faces. The cell dimensions were measured and are as follows:-

$\underline{a}$ = 31.78 ± 0.09 A.U.

$\underline{b}$ = 3.94 ± 0.01 A.U. β = 120.4° ± 0.2°

$\underline{c}$ = 23.84 ± 0.07 A.U.

Number of molecules in the unit cell = 8

Volume of the unit cell = 2574.0 A.U.^{3}

Calculated density = 1.405 g./cc.

Observed density (24.0°C) = 1.396 ± 0.004 g./cc.

The systematic absences observed were,

(hkl) absent when h+l is odd,

(h0l) absent when h is odd.

The space-group may be either Cc or C2/c. No deduction can be made between the alternative space-groups on the evidence so far obtained.

(j) 2'-Methyl 1:2-Benzanthraquinone.

The crystals, as provided, were long yellow-coloured needles of rather poor quality. On recrystallisation from the solvent (methyl ethyl ketone), which was used to purify them, a different crystal form was obtained. The recrystallisation was carried out at room temperature and the crystals obtained were needle shaped and light-brown in colour. After many attempts crystals of the original type were obtained when the recrystallisation was carried out at a temperature near 0°C. Both forms of crystal were examined and the data for each is given below.

(i) 1st Form - Yellow needles.

The crystals were found to be monoclinic with the needle axis as the unique axis **b**. The axial lengths **a** and **c** and the angle β were measured on the Geiger counter spectrometer. The cell dimensions are:-

$\underline{a}$ = 20.674 ± 0.020 A.U.

$\underline{b}$ = 4.06 ± 0.02 A.U. β = 90.8° ± 0.05°

$\underline{c}$ = 7.768 ± 0.008 A.U.

Number of molecules per unit cell	= 2
Volume of unit cell	= 652.0 A.U.^{3}
Calculated density	= 1.386 g./cc.
Observed density (23.5°C)	= 1.380 ± 0.004 g./cc.

The only systematic absences were,

(0k0) absent when k is odd.

The space-group is therefore $P2_1$ or $P2_1/\underline{m}$. However $P2_1/\underline{m}$ requires a reflected molecule at (0½0) as well as at (000) and an axial length for $\underline{b}$ of 4.06 A.U. will not permit this. Therefore the space-group is $P2_1$.

(ii) <u>2nd Form</u> - Light-brown needles.

The crystals were found to be monoclinic prismatic with cell dimensions as follows:-

$\underline{a}$ = 7.87 ± 0.02 A.U.

$\underline{b}$ = 16.53 ± 0.05 A.U. β = 113.5° ± 0.2°

$\underline{c}$ = 22.35 ± 0.06 A.U.

Number of molecules in the unit cell	= 8
Volume of the unit cell	= 2667.4 A.U.^{3}
Calculated density	= 1.357 g./cc.
Observed density (22.0°C)	= 1.353 ± 0.004 g./cc.

The systematic absences observed were,

(hol) absent when l is odd,

(oko) absent when k is odd.

The space-group is therefore $P2_1/c$. This space-group requires 4 asymmetric units per unit cell and hence the asymmetric unit must consist of two molecules.

(k) 3'-Methyl 1:2-Benzanthraquinone.

This compound was recrystallised from methyl ethyl ketone. Orange-coloured needles were obtained in the form of a spherulitic growth. The crystals, which were of poor quality, were found to be orthorhombic and the needle axis was taken as the c - axis. The cell dimensions were measured and are as follows:-

a = 21.93 ± 0.06 A.U.

b = 30.75 ± 0.09 A.U.

c = 3.95 ± 0.01 A.U.

Number of molecules per unit cell	= 8
Volume of unit cell	= 2663.6 $A.U.^3$
Calculated density	= 1.360 g./cc.
Observed density (22.3°C)	= 1.369 ± 0.004 g./cc.

The systematic absences observed were,

(okl) absent when k+l is odd,

(hko) absent when h is odd.

The space-group may be $Pn2_1a$ or $Pnma$ and no distinction can be made between these alternative space-groups on the above evidence.

(1) 4'-Methyl 1:2-Benzanthraquinone.

Many attempts were made, using different solvents, to obtain crystals of the above compound which were large enough to enable measurements to be carried out. Unfortunately all efforts proved unsuccessful and accordingly no observations were made on the space-group and the unit cell dimensions.

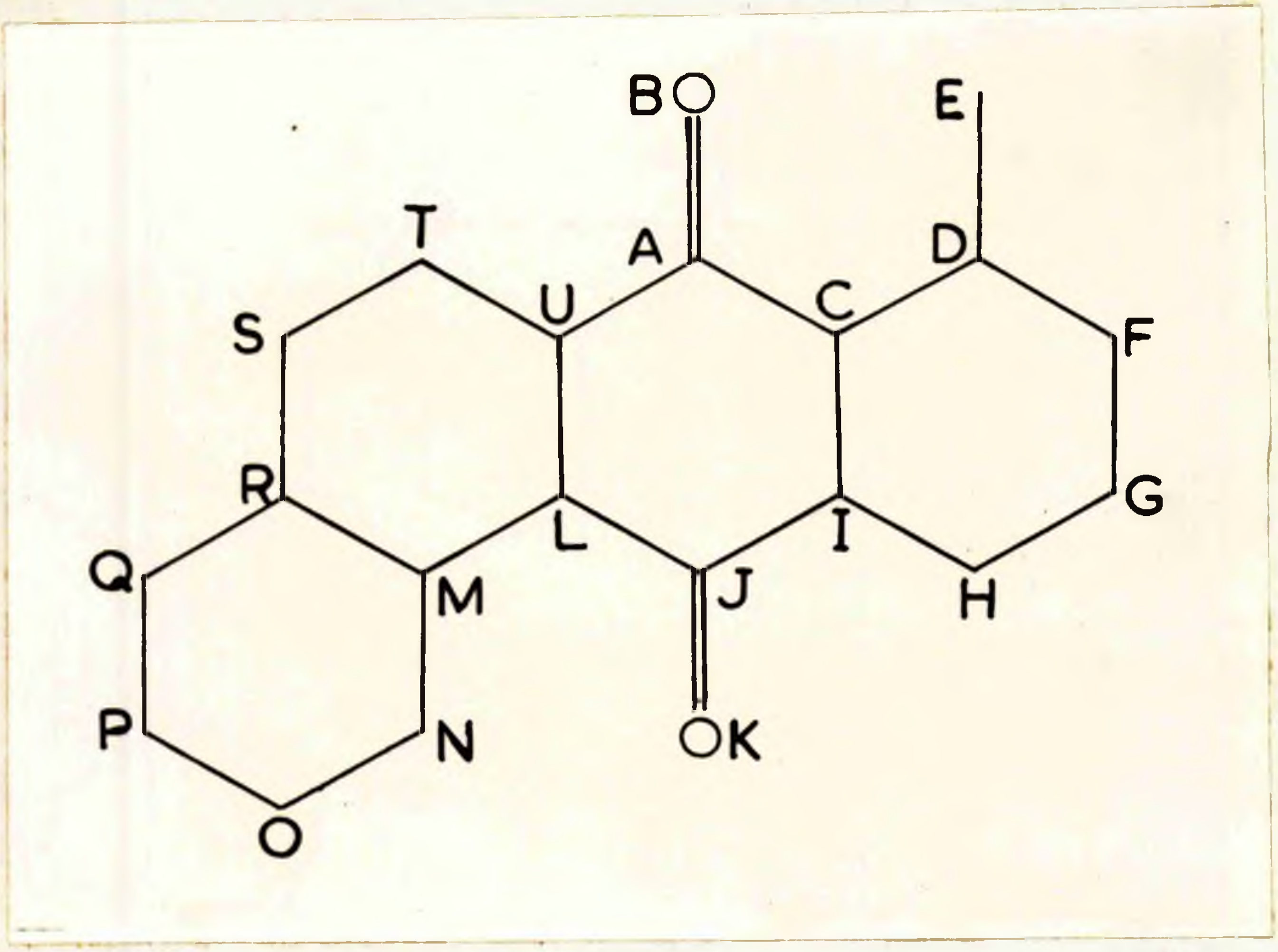


Fig. 3.1. The molecule of 5-methyl 1:2-benzanthraquinone ($C_{19}O_2H_{12}$), showing the lettering of the atoms adopted in this investigation.

CHAPTER III.

THE STRUCTURE OF 5-METHYL 1:2-BENZANTHRAQUINONE ($C_{19}O_2H_{12}$).

(a) Preliminary Discussion.

A sketch of the molecule is shown in Fig. 3,1. The indexing, as indicated by the lettering in this diagram, will be followed throughout this chapter.

The details of the determination of the space-group and unit cell dimensions are given in Chapter II, section (d). The space-group is P2$_1$nb and the axial lengths are,

a = 14.13 ± 0.01 A.U.

b = 23.27 ± 0.02 A.U.

c = 3.94 ± 0.01 A.U.

There are 4 molecules in the unit cell, the molecular weight is 272.26 and F(000) = 568.

The molecule has no centre of symmetry and hence the asymmetric unit is one molecule, consisting of 19 carbon atoms, 2 oxygen atoms and 12 hydrogen atoms. Neglecting the hydrogen atoms the asymmetric unit will be defined by 63 positional parameters.

Equi-inclination Weissenberg photographs were taken about the following axes of rotation - a, b, c, (401):(010). The upper layer lines recorded were as follows, layer lines one to seven of the a - axis,

layer lines one and two of the c - axis,

layer lines one to four of the (401):(010) - axis.

From the photographs of these zero and upper layer lines it was found possible to estimate the intensity of all the reflections which could be observed using copper K radiation. The dimensions of the crystal used to record the a - axis zero and upper layers were, 0.32 x 0.07 x 0.27 mm., where 0.27 mm., was the length of the crystal in the direction of the rotation axis a. The dimensions of the crystal used to record the zero, first and second layers of the c - axis were, 0.25 x 0.09 x 0.82 mm., where the largest dimension represents the length of the crystal along the needle axis c. The intensities recorded from all layers of the a and c - axes were corrected for absorption by the method due to Albrecht (Albrecht, 1939). The crystal sizes were such that no absorption corrections were required for the other intensities which were measured. All the intensities were measured visually by two independent observers and the intensities of the (hk0), (h0l) and (0kl) zones were also measured on the Geiger counter spectrometer.

The intensities of the equatorial layers were corrected for the usual Lorentz and polarisation factors and the relative values of $|F_o(hkl)|^2$ were obtained. An attempt was made to put the relative structure factors of the (hk0) zone on the absolute scale using Wilson's method, (Wilson, 1942).

In this method $\log_e \langle f^2 \rangle / \langle |F_o(hkl)|^2 \rangle$ is plotted against $\sin^2\theta/\lambda^2$ over ranges of $\sin^2\theta/\lambda^2$, $\langle f^2 \rangle$ being mean of the squares of the scattering factors for the planes within the specified range of $\sin^2\theta/\lambda^2$ and $\langle |F_o(hkl)|^2 \rangle$ the average of the squares of the structure factors of these planes. The resulting graph should be a straight line. The intercept of the graph gives the scale factor and the slope determines the appropriate temperature factor.

In the case of the (hk0) zone of 5-methyl 1:2-benzanthraquinone, the results were disappointing. The scatter of points on the resulting graph was such that no conclusion could be made regarding either the scale or the temperature factor. The reason for the apparent failure of Wilson's method is difficult to find. The number of reflections in each group was approximately 30, which would seem to be a sufficient number to give a reasonable statistical distribution. Moreover in this projection all the atoms are well resolved. After the failure of Wilson's method, it was decided to leave the structure factors on the relative scale and to determine the correct scale by comparison with the calculated structure factors.

The contribution of the hydrogen atoms to the calculated structure factors was neglected in the early stages of the investigation and an oxygen atom was assumed to have a scattering power $^4/_3$ that of a carbon atom. The carbon scattering curve used was that of Bergúis et. al. (Bergúis et. al., 1955). Account was taken of the thermal motion of the atoms by applying a correction factor exp. ($- B\sin^2\theta/\lambda^2$), where B is the temperature factor. In the initial stages the value of B was taken to be 3.7 A.U.^{2}. The equation for the calculated structure factor then becomes,

$F = 4$ (number of molecules in the unit cell) $\times f_c \times (S_c + {}^4/3\ S_o)$ where f_c is the scattering factor for carbon, suitably adjusted for the temperature effect, and S_c and S_o are the geometric factors for the carbon and oxygen atoms respectively. S_c and S_o are calculated from the postulated atomic co-ordinates.

The upper layer line intensities were corrected using the chart prepared by Cochran (Cochran, 1948). The intensities were put on the same relative scale by comparison with those corrected zero layer intensity values of reflections which also occur on upper layer photographs.

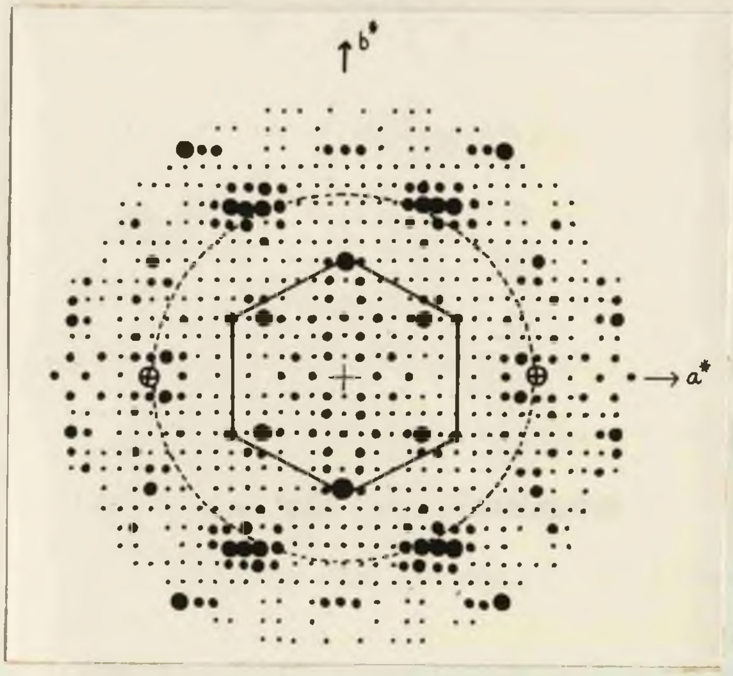
(b) Weighted Reciprocal Lattice Theory.

The concept of reciprocal space was first applied to crystallography by Ewald (Ewald, 1921). Each set of crystal planes is represented by a point in reciprocal space and the resulting mesh of points is called a reciprocal lattice. When the points on a scale drawing of the reciprocal lattice are weighted in accordance with the values of $|F_o(hkl)|^2$ of the reflections, the resulting lattice is known as a weighted reciprocal lattice. The scale used in drawing the reciprocal lattice was 5 cm./A.U.$^{-1}$. Lipson and Taylor (Lipson and Taylor, 1951) have stated that, in producing an optical transform of the atoms in a number of unit cells, one is merely reproducing the weighted reciprocal lattice. A better approximation to the optical transform is obtained if, on the reciprocal lattice, the planes are weighted in accordance with their unitary structure factors, thereby correcting for the change in scattering factor with the angle θ (Hanson, Lipson and Taylor, 1953). The unitary structure factor is defined by,;

$$U(hkl) = |F_o(hkl)| \Big/ \hat{f}(hkl) \times F(000)$$

where $\hat{f}(hkl)$ is the scattering factor for the plane, normalised to refer to an atom of unit electron content. Throughout this thesis all reciprocal lattices will be weighted in this manner.

It has been shown, (Hanson, Lipson and Taylor, 1952) that a considerable amount of information can be derived directly from the weighted reciprocal lattice. The Fourier transform of a regular hexagonal arrangement of atoms will have six main peaks with hexagonal symmetry. If a molecule consists essentially of benzene rings joined together, as is the case in the compound under discussion, and if the molecule lies in the plane of the projection, then, in the weighted reciprocal lattice of the projection, the main peaks will lie at equal intervals around a circle with centre the origin and radius 0.83 A.U.$^{-1}$. This is the "benzene circle". If the molecule is tilted out of the plane of the projection, the groups will move away from the circle. By finding the centres of gravity of the benzene



(a.)

(b.)

(c.)

<u>Fig. 3.2.</u> (a) The (hk0) weighted reciprocal lattice of 5-methyl 1:2-benzanthraquinone.

(b) The optical transform of the correct trial structure in the (hk0) projection.

(c) The optical transform of the (hk0) projection of the final structure.

ring groups concerned it should be possible to reconstruct the "mean" benzene ring which is the basis of the structure. The main difficulty in determining the orientation of the benzene ring from weighted reciprocal lattices is that if the tilt of the molecule is too great, some of the groups will lie outside the sphere of reflection for copper Kα radiation. Also, once the orientation of the mean benzene ring has been determined, it is still necessary to fit the benzene rings together to give the molecule. In general there are several ways in which this can be done and finding the correct one may take a considerable time.

The unit cell of 5-methyl 1:2-benzanthraquinone has one short axis (c - axis) of 3.94 A.U. It was expected therefore, that in the c - axis projection, the atoms would be well resolved, because the molecules cannot be tilted very far out of the plane of the projection and this was later confirmed. The only axial zone weighted reciprocal lattice which gave any information as regards the tilt of the molecule, was that of the (hk0) projection and a drawing of this weighted reciprocal lattice is shown in Fig. 3,2(a). In weighting this reciprocal lattice the relative values of $\frac{F_o}{f}$ were used, because the correct scale factor for the observed structure factors was not known.

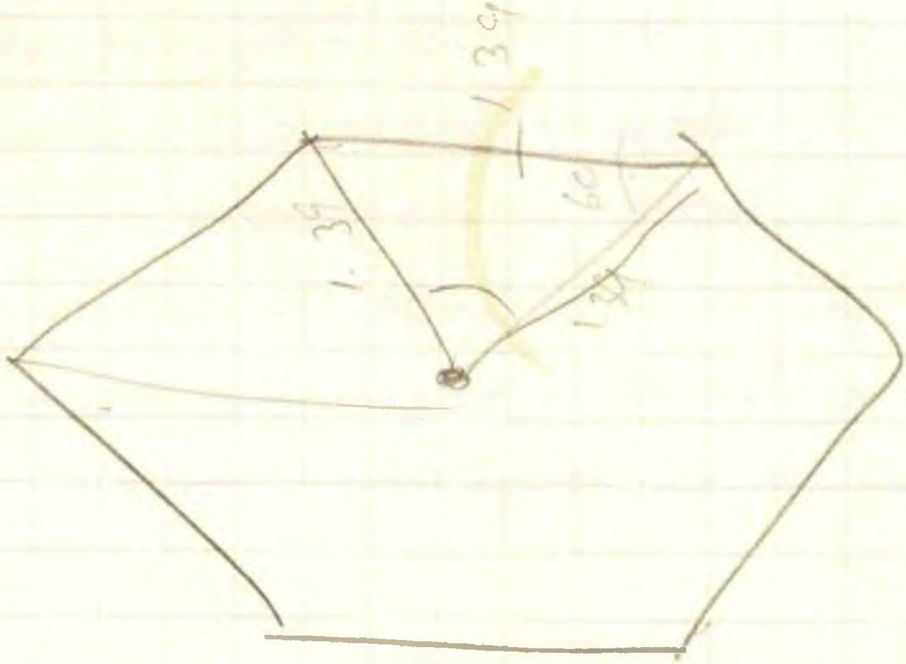
In the (hk0) projection there are two pairs of molecules which are mirror images. Accordingly it was expected that 12 benzene ring groups would be seen in the weighted reciprocal lattice. In fact, 10 — 10,000

$10^1 \rightarrow 10^4$

10 — 31
32 — 100
101 — 319
320 — 1000
1000 — 3200

10 — 40	1
40 — 160	2
160 — 640	3
640 — 2560	4
2560 — 10500	5

.38



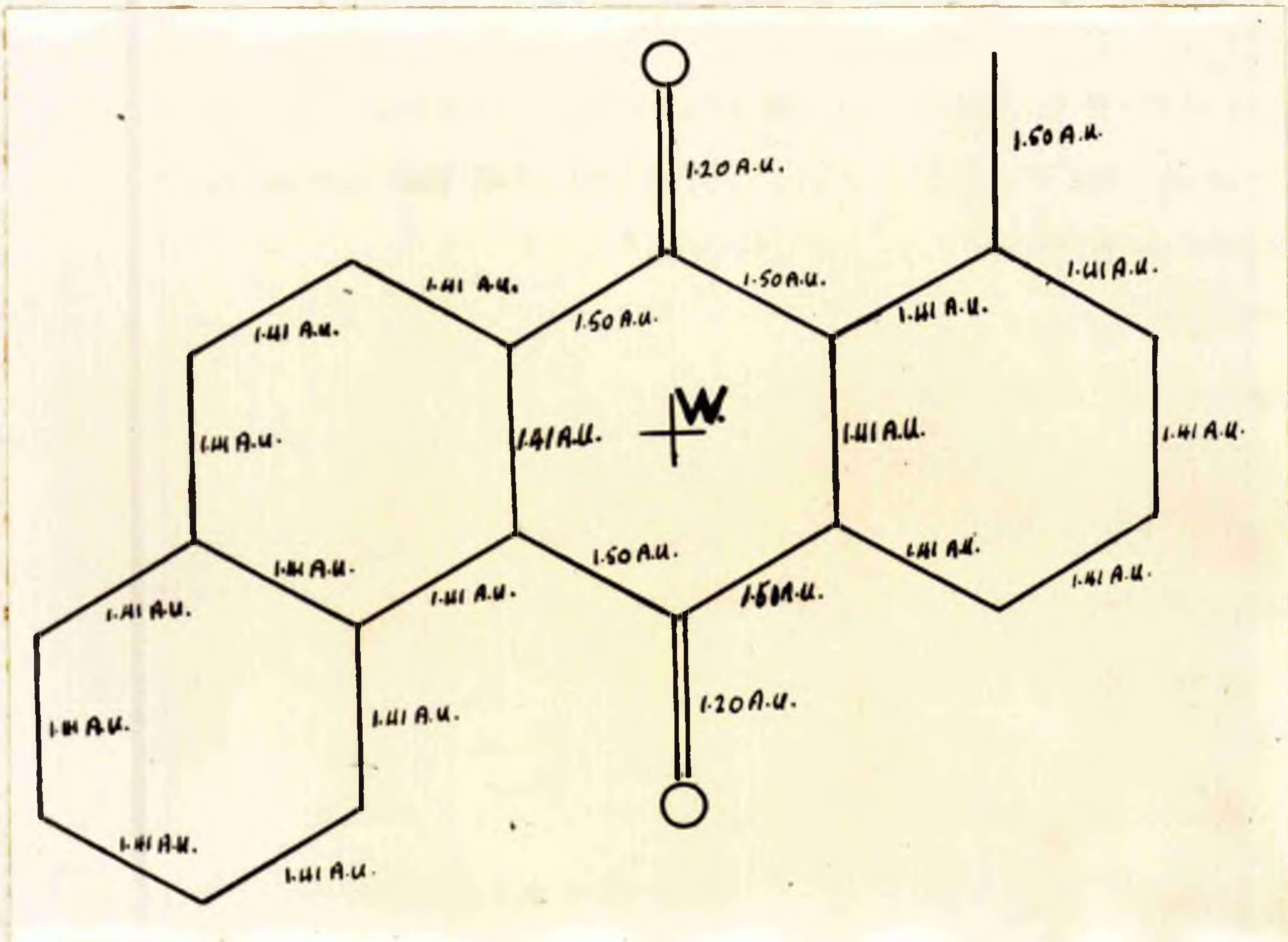


Fig. 3.3. The molecular model adopted in the initial stages of the investigation.

as can be seen from Fig. 3,2(a), there are only six groups although the groups are "spread out" to a certain extent. This means that the benzene rings of the molecules, related by the mirror plane, have the same orientation or orientations which differ by only a few degrees. The centres of gravity of the groups were determined and the mean benzene ring was calculated. This indicated that the molecules were tilted through an angle of approximately 25° about a line parallel to the a - axis.

(c) Determination of the Approximate Structure.

As stated earlier, it was expected that the only projection in which the atoms would be resolved was the c - axis projection. It was decided therefore to concentrate on this projection and to use the information derived from the weighted reciprocal lattice to attempt to find an approximate structure by trial and error methods. The c - axis projection is unfortunately non-centrosymmetric, which meant that, once the approximate structure had been derived, the subsequent determination of the accurate structure was a very slow process, because both the atomic parameters and the phases of the structure factors had to be refined.

The basic molecular model used in the initial stages is shown in Fig. 3,3. The point W will be referred to as the molecular origin throughout this chapter. The location of the molecule along the b - axis must be determined, but the molecule can be placed anywhere

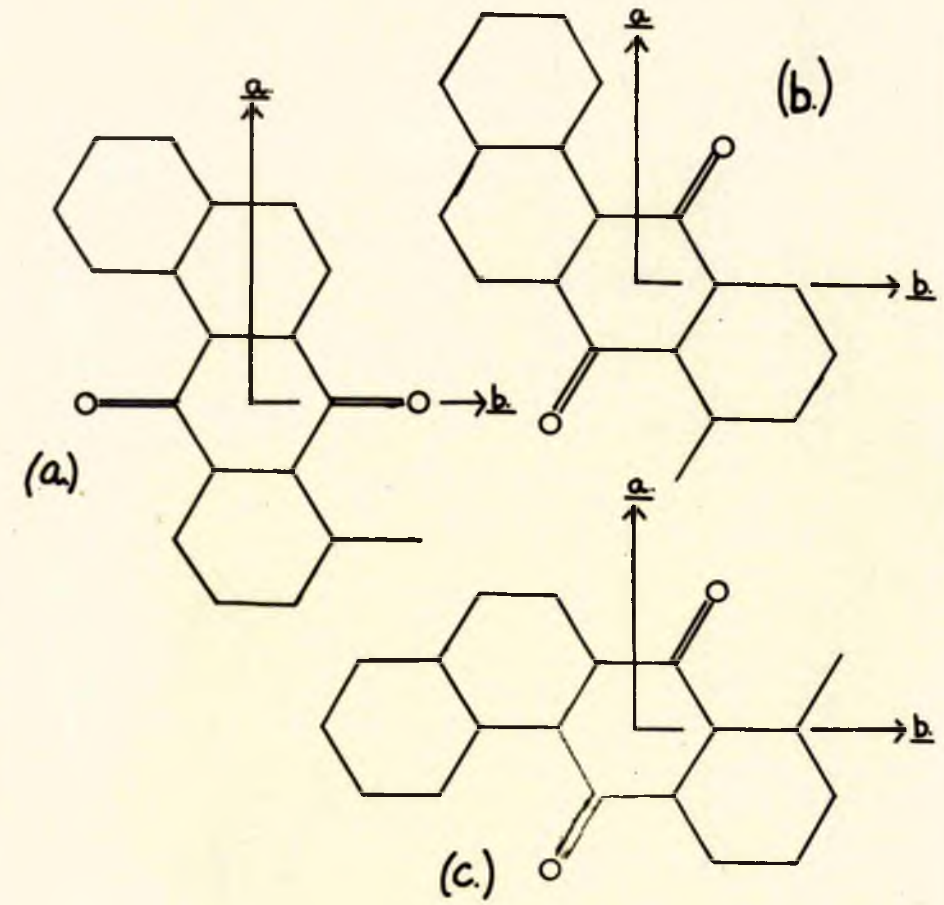


Fig. 3.4. (a), (b) and (c) show the three possible ways in which the molecule can be built up from the basic benzene ring derived from the (hk0) weighted reciprocal lattice.

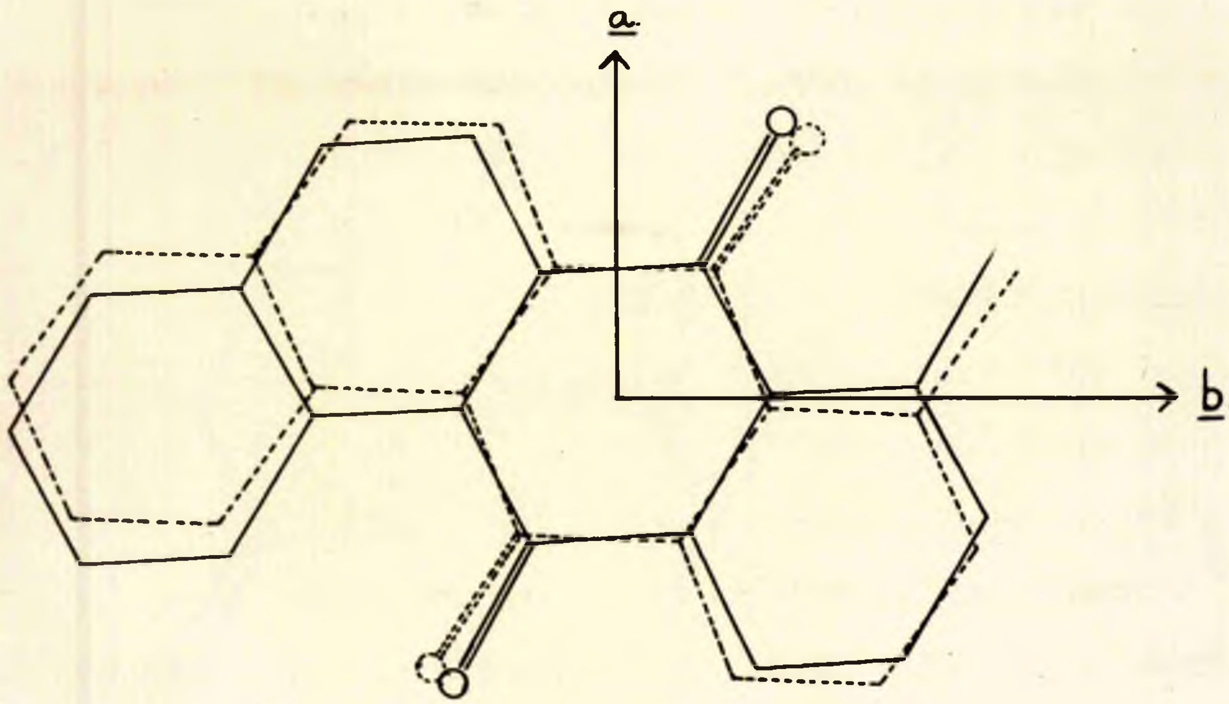


Fig. 3.5(a),(b). The molecules represented by (a) the solid line and (b) dotted line show the possible orientations of the molecule in the (hk0) projection.

along the a - axis because a is a screw-axis. This latter fact was used to determine the correct orientation of the molecule.

Assuming that the benzene rings of the pairs of molecules which are mirror images have the same orientation, then there are only three possible ways in which the benzene rings can be fitted together to give the molecule of 5-methyl 1:2-benzanthraquinone and these are shown in Fig. 3,4(a), (b) and (c). The tilt indicated by the weighted reciprocal lattice was applied to each molecule and the (h00) structure factors were calculated. An examination of the agreement between the observed and calculated structure factors showed that (c) in Fig. 3,4 was the correct molecule.

The agreement between the observed and calculated structure factors was examined when the molecule (Fig. 3,4(c)) was rotated through a few degrees about the c - axis. Good axial agreement was obtained in two positions, (1) when the molecule was rotated through 1.5° in a clockwise direction and (2) on a rotation of 2.5° in an anti-clockwise direction (Fig. 3,5). Using the Bragg structure factor machine the (0k0) structure factors were calculated for various positions of the molecular centre along the b - axis. For each of the two molecules, the best agreement was obtained with the molecular centre $\frac{1}{8}^{th}$ of the way along the b - axis. It was decided to investigate the orientation, indicated by (1) above, first. The axial structure factors were calculated and when a scale factor of 2.0 was applied to the observed structure factors, the reliability indices were found to be,

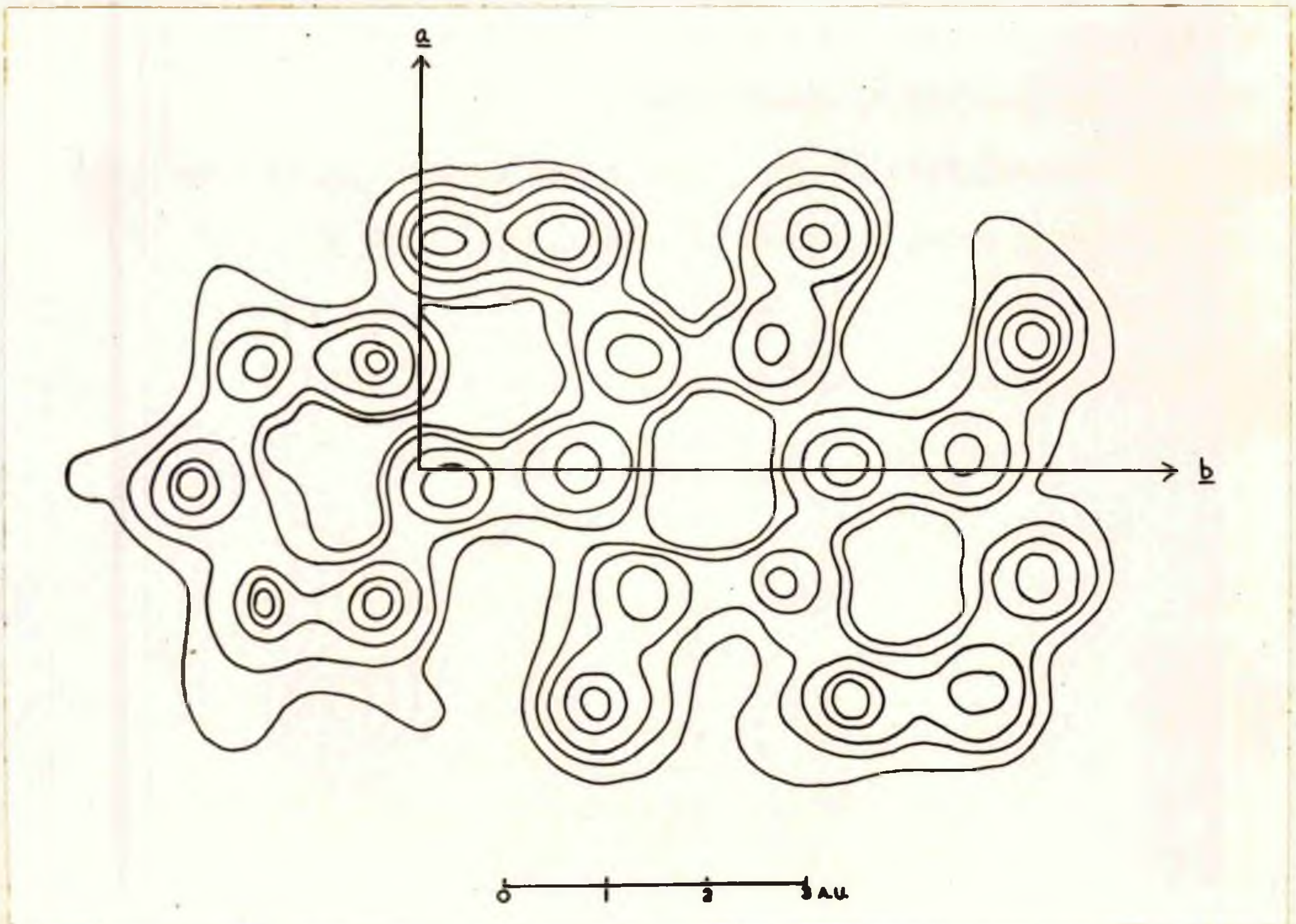
R(h00) = 0.20 (h = 0,2,.....,14) and R(0k0) = 0.20 (k = 0,2,.....,14)
A mask of the proposed structure was punched and the optical transform showed reasonable agreement with the weighted reciprocal lattice. Since it was expected that the structure was only approximate, the values of the 35 largest structure factors were calculated and an overall reliability index of 0.24 was obtained. At this stage a Fourier synthesis was computed using the observed structure factors and the phases derived from the calculated structure factors. The Fourier map was drawn and the new co-ordinates extracted with some difficulty. The structure factors were recalculated and the agreement between the observed and calculated structure factors was found to be worse and the model was abandoned.

The other possible orientation of the molecule was now investigated. The molecular centre was placed at (0.000 a, 0.125 b) and the atomic co-ordinates of the molecule are shown in Table 3,1. The optical transform of this proposed structure gave reasonable agreement with the weighted reciprocal lattice (see Fig. 3,2(a) and (b)) and the values of the 65 largest structure factors were calculated. The temperature factor used was B = 3.7 A.U.^{2} and a scale factor of 1.90 was applied to the observed structure factors. Apart from the structure factors F(1,12,0) and F(6,18,0) which were calculating much too low and the F(080) which was calculating too high, the agreement between the observed and calculated structure factors was remarkably good. Excluding these three structure factors the reliability index was 0.15.

TABLE 3.1

Fractional x and y co-ordinates.

ATOM.	x/a.	y/b.
B	0.167	0.171
K	-0.167	0.079
A	0.092	0.149
C	0.002	0.179
D	0.008	0.234
E	0.102	0.258
F	-0.072	0.263
G	-0.169	0.239
H	-0.169	0.185
I	-0.084	0.156
J	-0.092	0.098
L	-0.002	0.068
M	-0.007	0.014
N	-0.096	-0.012
O	-0.099	-0.064
P	-0.015	-0.094
Q	0.071	-0.070
R	0.077	-0.015
S	0.174	0.010
T	0.169	0.062
U	0.084	0.092



<u>Fig. 3.6.</u> The initial Fourier map of the molecule of 5-methyl 1:2-benzanthraquinone projected down the c - axis. The contours are drawn at arbitrary intervals of electron density.

This was regarded as very promising and consequently a Fourier synthesis was computed using the phases of 62 of these structure factors. The Fourier map giving the electron density distribution obtained is shown in Fig. 3,6 and the atomic positions are clearly defined as peaks in the electron density distribution.

The co-ordinates of the peaks in the Fourier map of Fig. 3,6 were extracted using the semi-analytical method of Burns and Iball (Burns and Iball, 1955). The values of the electron density at the nine points about the atomic positions are plotted on the mesh of the Fourier map, drawn on a larger scale. The maxima along the mesh lines are found using the tables prepared by Booth (Booth, 1948). The maxima are joined by two smooth curves and the intersection of the curves gives the position of the maximum in the electron density distribution.

The co-ordinates, as obtained from the electron density map, were used to calculate the structure factors of all the observed reflections in the (hk0) zone. From an examination of the structure factors, it appeared that the value of the temperature factor used (B = 3.7 A.U.^{2}) was too low and an attempt was made to find a more correct value. The ratio $\Sigma|F_o|^2/\Sigma|F_c|^2$ was found for equal ranges of $\sin^2\theta$, where

$$|F_c|^2 = |(S_c + \frac{4}{3} S_o)|^2 \times f_c^2 \times \exp.(-2B\sin^2\theta/\lambda^2)$$

S_c, S_o are the geometric factors for the carbons and oxygens respectively, f_c is the value of the scattering factor obtained from the theoretical Berghuis curve and $\exp.(-2B\sin^2\theta/\lambda^2)$ is the correction to the scattering curve for the temperature effect. The graph of $\log_e \Sigma|F_c|^2/\Sigma|F_o|^2$ against $\sin^2\theta/\lambda^2$ should give a straight line. The intercept will give the scale factor for the observed structure factors and the slope will give the correction to be applied to the temperature factor. The graph indicated a scale factor of approximately 1.90 and a temperature factor of 4.5 A.U.^{2}. The scatter of points on the graph was due to three factors:-

(1) the atomic co-ordinates at this stage were not very accurate,

(2) no account was taken of the hydrogen contribution to the scattering,

(3) the correct scattering curve for the oxygen atoms should have been used.

The structure factors were recalculated using a temperature factor $B = 4.5$ A.U.^{2} and on applying a scale factor of 1.80 to the observed structure factors, the reliability index over all the observed reflections was found to be 0.30. The phases derived from this calculation of structure factors were used to compute an $(F_o - F_c)$ Fourier synthesis. In this method a Fourier series is computed using as coefficients the differences between the observed and calculated structure factors. The gradients of this function at the atomic centres are determined from the figure field and the shift which must be applied to the nth atom is given by

$$r_n = -\left(\frac{\delta D}{\delta r}\right)_n C(\rho_c)$$

where $\left(\frac{\delta D}{\delta r}\right)_n$ is the gradient of the electron density at the n^{th} atomic centre and $C(\rho_c)$ is the curvature of ρ_c at this point. In practice ρ_c can be replaced by ρ_o and we can write

$$C(\rho_c) = C(\rho_o) = \left(\frac{\delta^2\rho_o}{\delta r^2}\right)_n$$

and if

$$\rho_o(r) = A\ \exp.(-pr^2)$$

is the expression for the electron density distribution at the peak, then

$$\left(\frac{\delta^2\rho_o}{\delta r^2}\right)_n = -2p(\rho_o)_n$$

Hence

$$\Delta r_n = \left(\frac{\delta D}{\delta r}\right)_n \Big/ 2p(\rho_o)_n$$

In the case of the compound under consideration, a difference Fourier synthesis should correct all carbon and oxygen positions and indicate whether or not the scale and temperature factors are correct. More-over, any errors due to series termination will be eliminated. If a set of values of F_c evaluated using only carbon and oxygen contributions are subtracted from the F_o values then, in theory, only the hydrogen contributions will remain and hence a difference Fourier synthesis can be used to estimate hydrogen positions. In the case of a non-centrosymmetric zone it has been shown that all shifts must be multiplied by a factor t, where

$t = 1$ if the structure is centrosymmetrical,

$1 < t < 2$ if the structure is non-centrosymmetrical, but certain of its projections are (Schomaker et. al., 1950),

$t = 2$ if the structure is completely non-centrosymmetric (Cruickshank, 1950).

The difference Fourier synthesis was computed for the (hk0) zone and the new co-ordinates were obtained from the resulting map of electron density. Since this crystal has only one centrosymmetric projection, it was decided to double all shifts. The optical diffraction pattern of this new structure was examined, but it did not exhibit any marked improvement in the agreement of the structure factors – F(080), F(6,18,0), F(1,12,0). An examination of these structure factors showed that, when all the y co-ordinates obtained from the difference Fourier were reduced by $^{y}/_{b} = 0.003$, the agreement between the observed and calculated values showed a marked improvement as shown in Table 3,2.

TABLE 3,2.

h	k	l	F'_c	F''_c	F_o
0	8	0	19.5	7.8	<1.4
1	12	0	3.1	22.3	33.4
6	18	0	2.4	24.6	33.6

F'_c are the calculated structure factors before the difference Fourier and F''_c are the values after the overall shift was applied. The new co-ordinates which are listed in Table 3,3 were used to recalculate

TABLE 3.3

Fractional x and y co-ordinates.

ATOM.	x/a.	y/b.
B	0.172	0.165
K	-0.172	0.076
A	0.100	0.151
C	0.003	0.186
D	0.010	0.234
E	0.100	0.260
F	-0.083	0.256
G	-0.157	0.237
H	-0.172	0.183
I	-0.078	0.158
J	-0.090	0.090
L	0.005	0.062
M	-0.007	0.005
N	-0.097	-0.015
O	-0.105	-0.068
P	-0.017	-0.109
Q	0.074	-0.081
R	0.078	-0.026
S	0.165	0.008
T	0.170	0.058
U	0.084	0.085

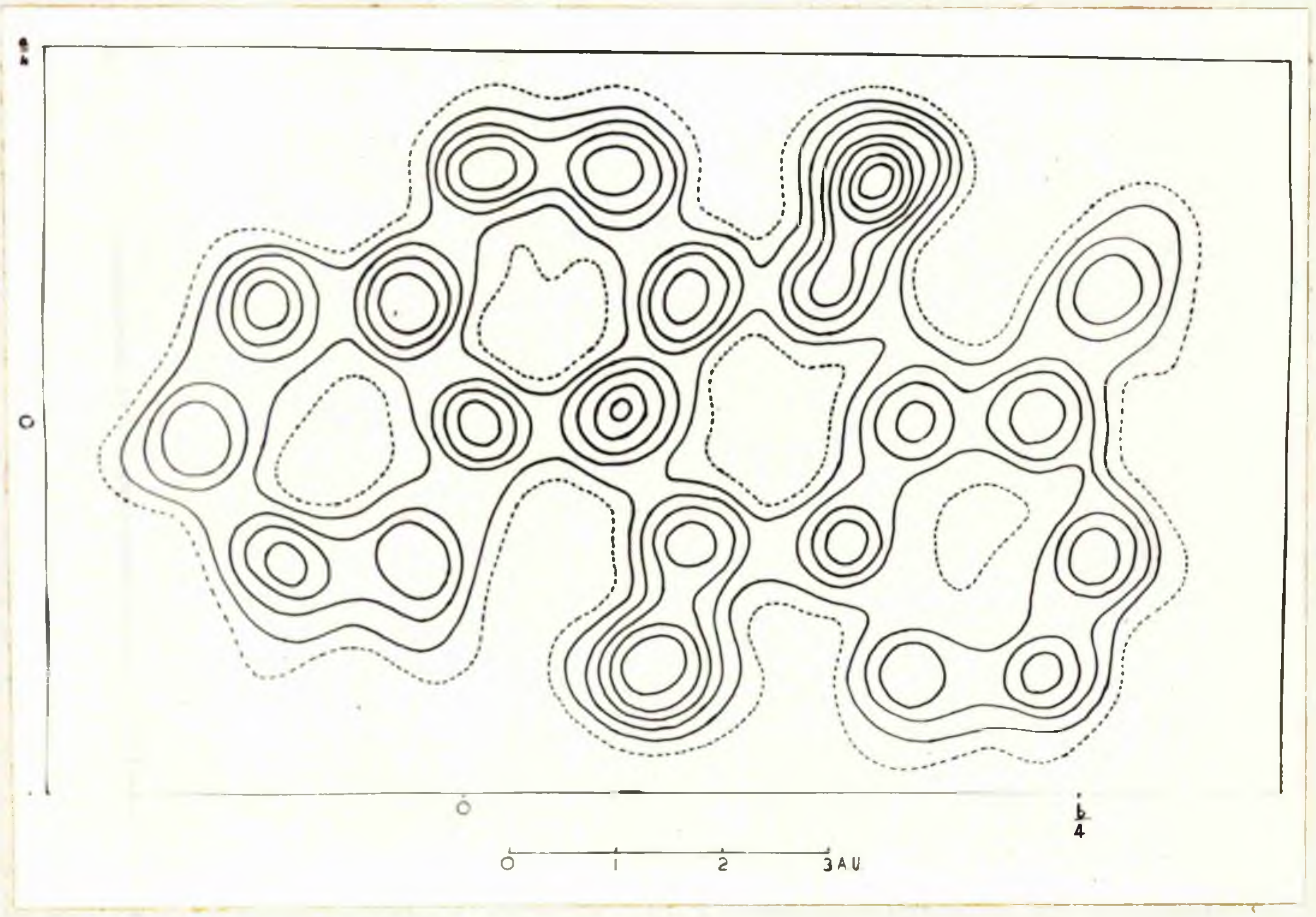


__Fig. 3.7.__ The Second Fourier map of the molecule of 5-methyl 1:2-benzanthraquinone projected down the __c__ - axis. The contours are drawn at intervals of 1 e./A.U.^{2}.

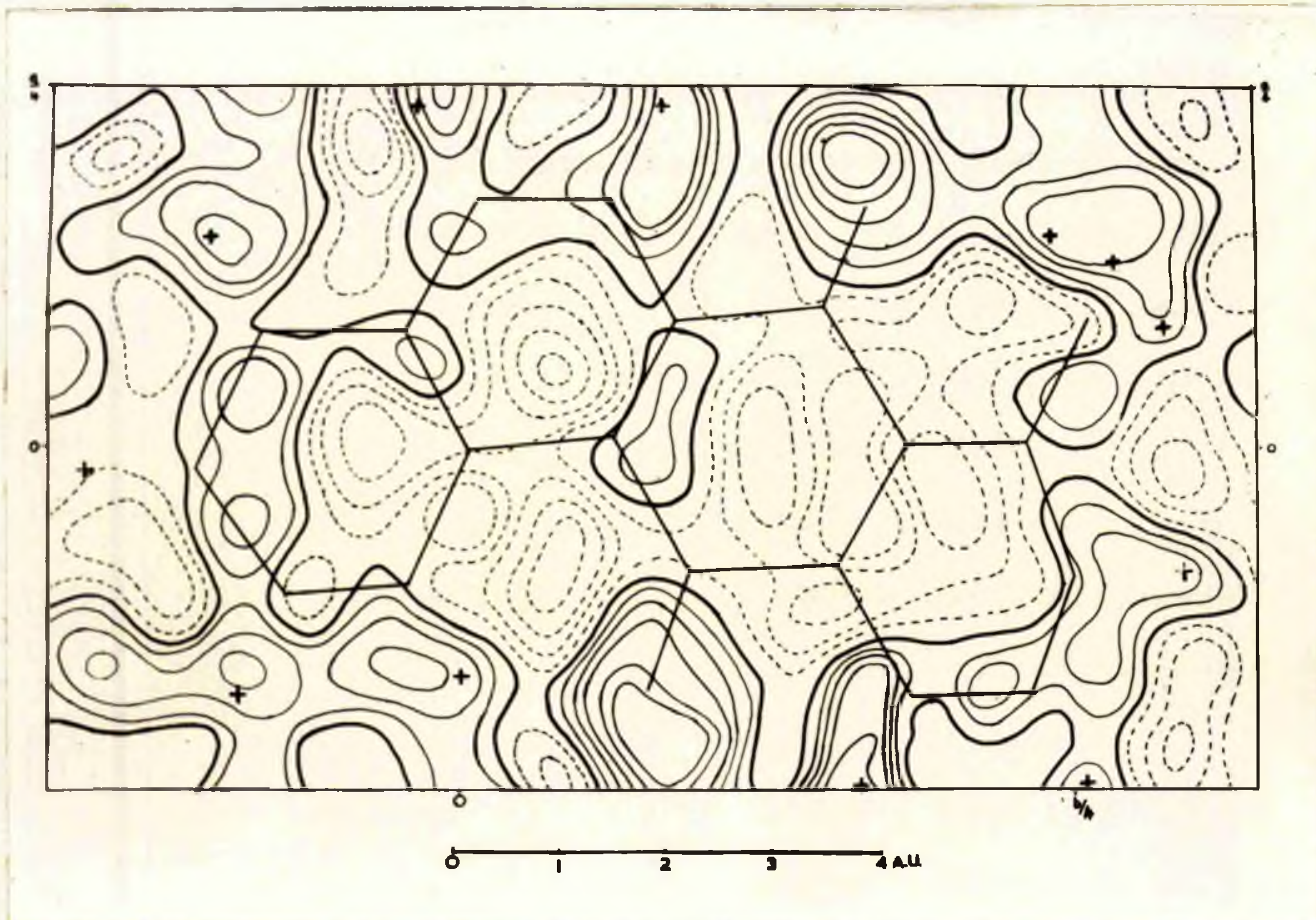


Fig. 1.8. The (F_o − $F_{\text{carbon and oxygen}}$) Fourier projection down the c − axis. The contours are at intervals of 0.2 e./A.U.^{2} the zero contour is the solid black line and the negative contours are dotted. The calculated hydrogen atom positions are indicated by +.

the structure factors of all the observed reflections with sin $\leqslant 0.6$ together with those reflections outside this limit, which had high F_o values. The reliability index was 0.23 compared with 0.26 for the corresponding structure factors on the previous calculation. A Fourier synthesis was computed using the calculated phases and a well resolved electron density map was obtained (Fig. 3,7). The new atomic co-ordinates were extracted using the Burns and Iball method and the structure factors for the whole (hk0) zone were recalculated and the reliability index was found to be 0.23. This reliability index included the values of $(F_o - F_c)$ for the unobserved reflections when F_c was greater than the maximum estimated value of F_o, and all the unobserved reflections were given half their maximum value in the summation ΣF_o.

A difference Fourier synthesis was now computed using the phases of all the observed structure factors. The resulting map of electron density is shown in Fig. 3,8. The hydrogen positions F', G', H', N', O', P', Q', S', T', calculated on the assumption of a carbon-hydrogen bond length of 1.05 A.U., are marked by crosses and with one exception (F') agree fairly well with the observed electron density distribution. The positions of the hydrogen atoms of the methyl group were estimated from the electron density contours and are shown marked with crosses. The double shifts were calculated and the new co-ordinates obtained are shown in Table 3,4. In the difference Fourier map the positions

TABLE 3.4.

Fractional x and y co-ordinates.

ATOM.	x/a.	y/b.
B	0.167	0.165
K	-0.165	0.077
A	0.100	0.149
C	0.004	0.181
D	0.004	0.231
E	0.043	0.257
F	-0.086	0.257
G	-0.169	0.233
H	-0.168	0.182
I	-0.076	0.154
J	-0.086	0.093
L	0.004	0.063
M	-0.005	0.011
N	-0.095	-0.021
O	-0.100	-0.072
P	-0.014	-0.107
Q	0.075	-0.081
R	0.077	-0.022
S	0.168	0.006
T	0.171	0.061
U	0.085	0.088

of the oxygen atoms are in regions of relatively high electron density. This indicated that the temperature factor was too high and hence in the recalculation of the structure factors the contribution of the oxygen atoms was calculated separately. The oxygen scattering curve used was that of Berghuis et. al., (1955) with a temperature correction of exp.$(-B\sin^2\theta/\lambda^2)$, where B = 3.7 A.U.^{2}. The structure factors were recalculated with and without the hydrogen contribution and the corresponding R factors were,

R(hk0) = 0.21 (without hydrogen contribution),

R(hk0) = 0.20 (including the hydrogen contribution).

At this stage it was decided to check that this was the correct structure by investigating the (0kl) zone. The z co-ordinates were calculated on the assumption that in the (hk0) projection the molecule was tilted through an angle of 26° about a line parallel to the a - axis. The first stage was to determine the position of the molecular centre along the c - axis. This was done by calculating the structure factors F(002), F(004), F(062), for various positions of the molecular centre from $^Z/_c$ = 0 to $^Z/_c$ = 0.5. When the molecular centre was placed at $^Z/_c$ = 0.09, the agreement between the observed and calculated structure factors was quite good and the atomic Z co-ordinates in this position are listed in Table 3,5. The structure factors of all the observed reflections in the (0kl) zone were calculated and reliability index was found to be 0.23. The phases derived from this calculation were used to compute a Fourier synthesis and the resulting electron density map

TABLE 3.5.

Fractional z co-ordinates.

ATOM.	z/c.
B	0.204
K	-0.046
A	0.157
C	0.253
D	0.390
E	0.463
F	0.462
G	0.400
H	0.259
I	0.172
J	0.000
L	-0.090
M	-0.252
N	-0.326
O	-0.469
P	-0.576
Q	-0.498
R	-0.332
S	-0.249
T	-0.097
U	-0.016

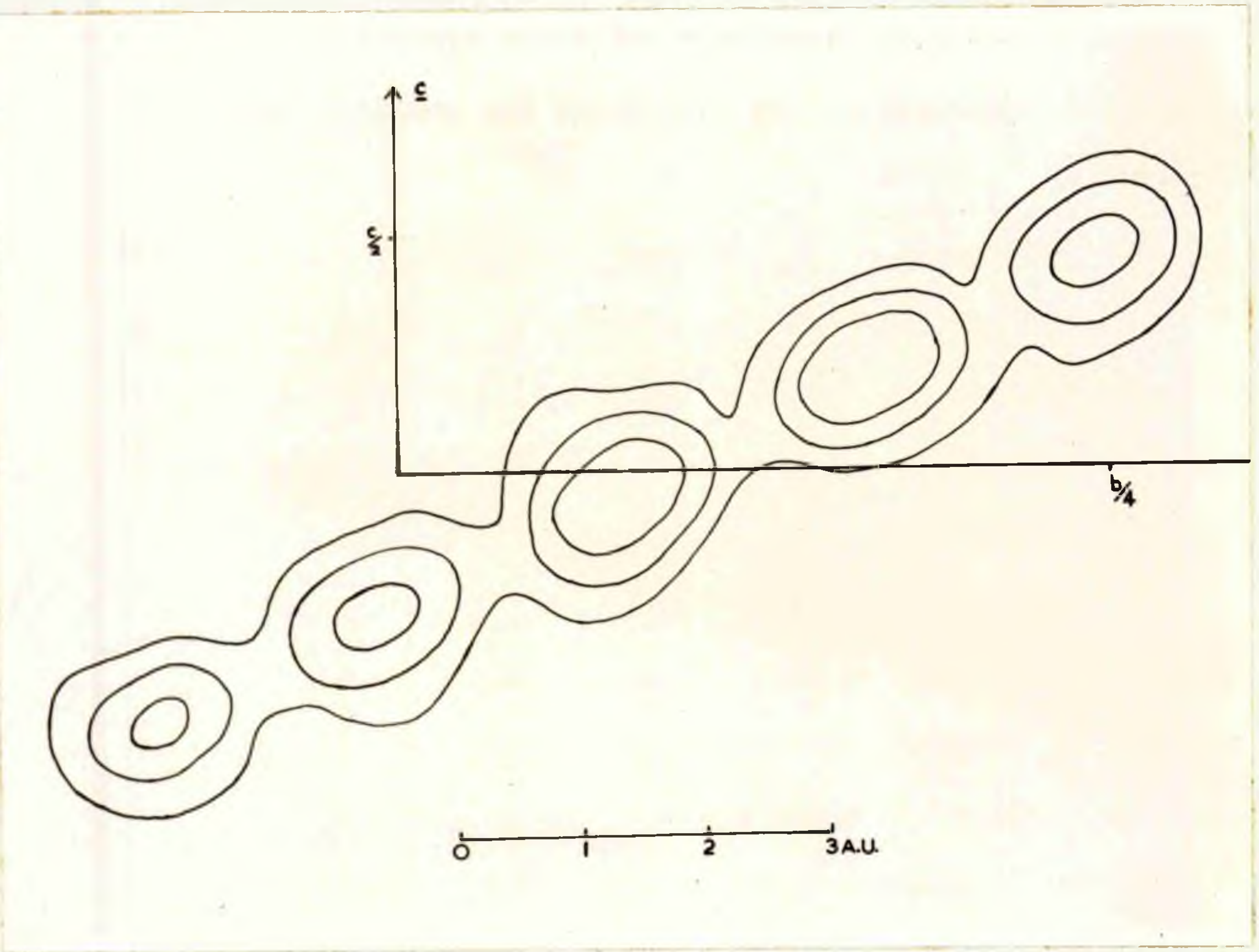


Fig. 3.9. The a - axis Fourier projection. The contours are drawn at arbitrary intervals.

is shown in Fig. 3,9. Although no atoms were resolved the general shape of the molecule in this projection was confirmed.

The structure factors of the few observed reflections of the (h0l) zone were also calculated and their agreement with the observed values was reasonable. At this point the structure was considered to be solved.

(d) The Refinement of the Structure of 5-Methyl 1:2-Benzanthraquinone.

It was clear that the refinement of this compound by desk computation would be a long and tedious process. It was decided to carry out the refinement by the method of least squares using electronic computing facilities.

The method of least squares was suggested by Hughes (Hughes, 1941). The theory of errors predicts that if the errors in the measured F_o's follow the normal or Gaussian law, then the best atomic parameters are those which minimise the quantity

$$R' = \sum_q w(hkl) \left\{ |F_o(hkl)| - |F_c(hkl)| \right\}^2 \qquad (1)$$

where $\sum_q$ denotes the sum over all independent terms and w(hkl) is the weight assigned to a particular value $F_o(hkl)$.

Atomic parameters on which R depends include not only atomic co-ordinates, but all quantities which affect the value of the calculated structure factors e.g. the temperature factors of the atoms. In deriving the least squares equations, only the effects of changes in atomic co-ordinates will be considered.

Small changes in atomic co-ordinates result in equations of the type

$$\Delta F_c = \sum_{n=1}^{N}\left(\frac{\delta F_c}{\delta x_n}\cdot\Delta x_n + \frac{\delta F_c}{\delta y_n}\cdot\Delta y_n + \frac{\delta F_c}{\delta z_n}\cdot\Delta z_n\right) \quad (2)$$

where Δx_n etc. are the errors in the position of the n^{th} atom. These equations can be solved for Δx_n etc. by the method of least squares. There will be as many equations of the type (2) as there are observed structure factors and, if a reasonable accuracy is to be desired, this number should be considerably greater than the number of independent co-ordinate corrections to be determined. If the molecule contains no centre of symmetry this number will be 3N. The set of equations (2) is reduced to a set of 3N equations called the Normal Equations. The n^{th} of these is formed by multiplying both sides of each equation, $\Delta F_c = F_o - F_c$, by $w\cdot\frac{\delta F_c}{\delta x_n}$ and adding the q right hand sides and the left hand sides, giving the equation.

$$\sum_q \omega\,(F_o - F_c)\cdot\frac{\delta F_c}{\delta x_n} = \sum_q \omega\left\{\left(\frac{\delta F_c}{\delta x_n}\right)^2\cdot\Delta x_n + \frac{\delta F_c}{\delta x_n}\cdot\frac{\delta F_c}{\delta y_n}\cdot\Delta y_n - \frac{\delta F_c}{\delta x_n}\cdot\frac{\delta F_c}{\delta z_n}\cdot\Delta z_n\right.$$

$$\left. + \sum_m \frac{\delta F_c}{\delta x_n}\left(\frac{\delta F_c}{\delta x_m}\cdot\Delta x_m + \frac{\delta F_c}{\delta y_m}\cdot\Delta y_m + \frac{\delta F_c}{\delta z_m}\cdot\Delta z_m\right)\right\} \quad (3)$$

where $\sum_m$ denotes the sum overall atoms except the n^{th}. In this way a set of 3N equations is obtained, which can be solved for the 3N unknown co-ordinate corrections. It can be shown that if the atoms are well resolved, quantities of the type

$$\sum_q w\,\frac{\delta F_c}{\delta x_n}\cdot\frac{\delta F_c}{\delta x_m}$$

are likely to be small compared with $\sum_q w\,\frac{\delta F_c}{\delta x_n}^2$. If the axes are orthogonal, or nearly so, quantities of the type $\sum_{q} w \frac{\delta F_c}{\delta x_n} \cdot \frac{\delta F_c}{\delta y_n}$ can also be neglected and equation (3) reduces to

$$\Delta x_n \sum_{q} w \left(\frac{\delta F_c}{\delta x_n}\right)^2 = \sum_{q} w(F_o - F_c) \cdot \frac{\delta F_c}{\delta x_n} \qquad (4)$$

The refinement of the (hk0) and (0kl) zones was carried out on the Pegasus computer at Northampton Polytechnic, using the least squares programme devised by Dr. J. Milledge. This programme enables equations of the type (4) to be solved. The (hk0) zone was refined first and the co-ordinates used in the initial structure factor calculation were those shown in Table 3,4. It was expected that in a planar structure of this type, the atoms at the centre of the molecule would vibrate much less than those on the outer rim and consequently would have a lower temperature factor B. It was also expected that those carbon atoms which had three carbon-carbon linkages would vibrate less than an atom with only two carbon-carbon linkages and one carbon-hydrogen linkage. The individual isotropic temperature factors assigned to the atoms are shown in Table 3,6.

TABLE 3,6.

Type	Atom	B (A.U.^{2})
Oxygen	B,K.	3.7
Carbon	A,C,I,L,M,R,U,J.	3.7
Carbon	D,F,G,H,J,N,O,P,Q,S,T.	4.6
Carbon	E.	5.0
Hydrogen	F',G',H',N',O',P',Q',S',T',E$_1'$,E$_2'$,E$_3'$	5.5

One cycle of least squares was carried out and the new co-ordinates were obtained. The programme did not refine the individual temperature factors, but only the overall temperature factor. The first cycle indicated that the latter was too low by a factor $\Delta B = 0.3$ A.U.^{2}. More-over at this time the structure of 1:5-dichloro-anthraquinone was published (Bailey, 1958) and the temperature factors quoted for the oxygen atoms were $B = 6.5$ A.U.^{2}. Therefore, before carrying out further cycles of least squares refinement, it was decided to redistribute the isotropic temperature factors. The new set of temperature factors are shown in Table 3,7.

TABLE 3.7.

Type	Atom	B (A.U.^{2})
Oxygen	B,K.	5.0
Carbon	A,C,I,L,M,R,U,J.	4.0
Carbon	D,F,G,H,N,O,P,Q,S,T.	4.5
Carbon	E.	5.0
Hydrogen	$F',G',H',N',O',P',Q',S',T',E',E'_2,E'_3,$	6.0

The structure factors were recalculated using the co-ordinates derived from the first cycle and the isotropic temperature factors listed in Table 3,7. The reliability index was reduced to $R = 0.142$ as compared with $R = 0.20$ before the first cycle. A further three cycles of least squares were computed. The reliability index of the structure factors on which the fourth cycle was carried out was $R = 0.13$.

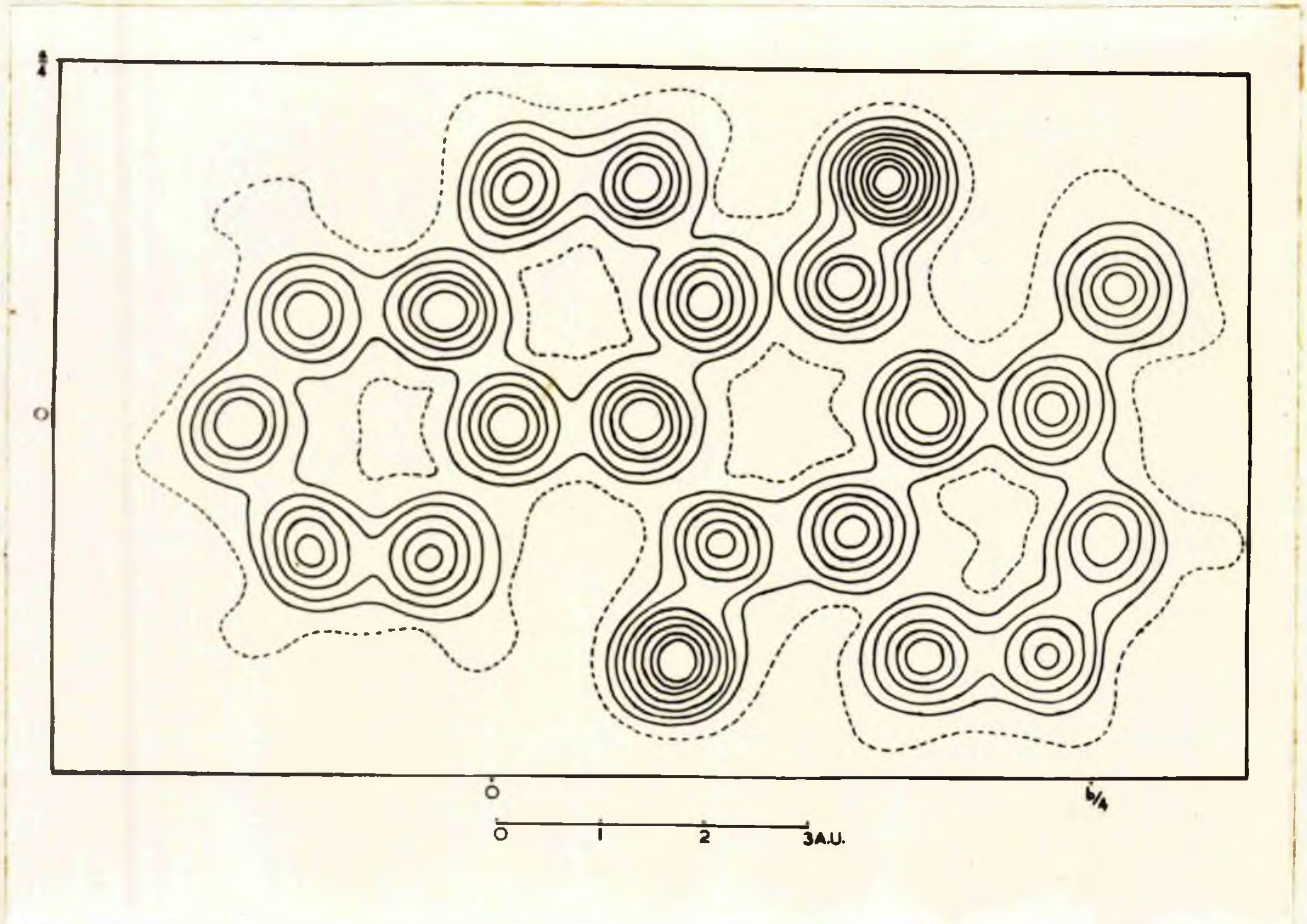


Fig. 3.10. Final c - axis Fourier projection. The contours are drawn at intervals of 1 e./A.U.^{2} and the 1 e./A.U.^{2} contour is dotted.

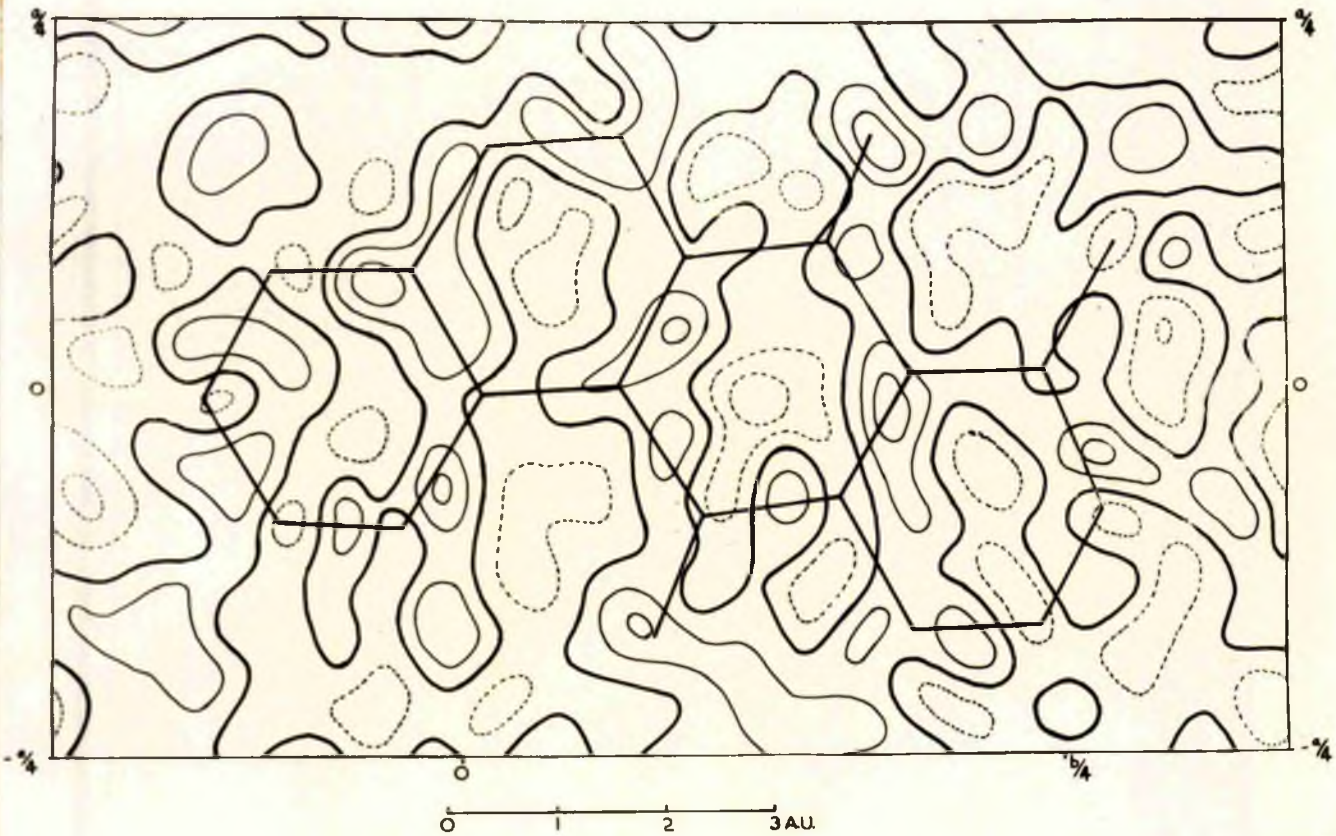


Fig. 3.11. **Final c - axis ($F_o - F_c$) Fourier projection.** **The contours** are drawn at intervals of 0.2 e./A.U.^{2}, the zero contour is the solid black line and the negative contours are dotted.

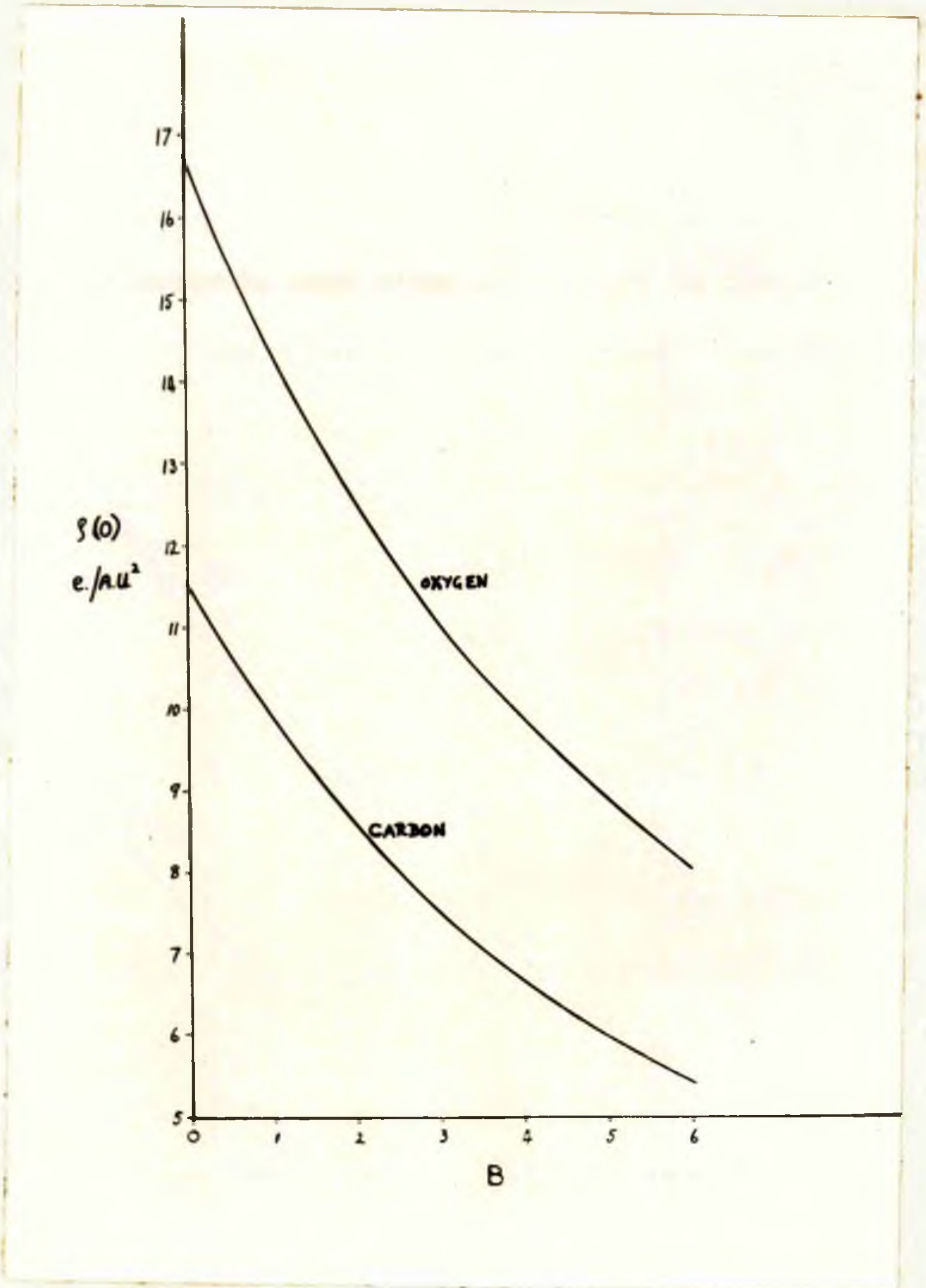


Fig. 3.12. Graph of electron density at the atomic peak (ρ(0)) against temperature factor (B) for a carbon and an oxygen atom.

The co-ordinate shifts during the four cycles are shown in Table 3,8(a) and (b). It was observed that for several atoms, the co-ordinate shifts were oscillating. In these cases the full shifts indicated at the end of the fourth cycle were adjusted to take account of the oscillation. The final set of x and y co-ordinates are shown in Table 3,9.

The phases derived from the last set of calculated structure factors were used to compute a final F_o Fourier synthesis and a final difference Fourier synthesis and the resulting contour maps of electron density are shown in Figs. 3,10 and 3,11. From these two maps an estimate was made of the individual isotropic temperature factors.

If the electron density distribution of an atom in projection is spherically symmetrical and can be represented by the function $\rho(r)$, then, if f(s) is the corresponding atomic scattering factor, it can be shown that

$$\rho(r) = \int_{0}^{S_o} 2\pi s.\ f(s).\ J_o(2\pi rs)ds.$$

where S_o is the radius of the limiting copper sphere. This equation can be solved by numerical integration. The carbon and oxygen scattering curves used were those of Berghuis et. al. and the values $\rho(0)$ of the eletron density at the atomic centre were derived when temperature factors of B = 1,2,......,6 were incorporated in the scattering curves. The graphs of $\rho(0)$ plotted against B are shown in Fig. 3,12.

TABLE 3.8.

x and y co-ordinate shifts after each cycle of least squares refinement of the (hk0) zone.

(a) x co-ordinate shifts in A.U.

ATOM	CYCLE I.	CYCLE II.	CYCLE III.	CYCLE IV.
B	0.0431	-0.0024	0.0051	-0.0027
K	-0.0759	0.0021	-0.0172	0.0062
A	-0.0390	-0.0065	-0.0057	-0.0095
C	0.0596	0.0291	0.0195	-0.0349
D	0.0496	-0.0122	0.0145	-0.0179
E	0.0747	0.0411	0.0103	0.0048
F	-0.0079	0.0318	-0.0071	0.0380
G	0.0784	0.0018	-0.0052	0.0023
H	0.0131	0.0052	-0.0034	0.0048
I	-0.0061	0.0016	-0.0339	0.0129
J	-0.0382	-0.0247	0.0072	-0.0059
L	-0.0788	0.0187	-0.0404	0.0220
M	-0.0408	0.0105	-0.0028	0.0232
N	-0.0408	-0.0009	-0.0153	0.0100
O	0.0619	0.0239	-0.0013	0.0233
P	0.0472	0.0326	-0.0030	0.0209
Q	-0.0168	-0.0211	0.0246	-0.0236
R	-0.0150	-0.0267	0.0291	-0.0277
S	-0.0790	0.0167	-0.0023	0.0034
T	0.0203	-0.0302	-0.0014	-0.0300
U	0.0281	-0.0268	0.0000	-0.0220

TABLE 3.8.

(b) y co-ordinate shifts in A.U.

ATOM.	CYCLE I.	CYCLE II.	CYCLE III.	CYCLE IV.
B	-0.0088	-0.0056	0.0033	0.0091
K	-0.0030	0.0056	-0.0056	0.0067
A	-0.0761	0.0230	-0.0132	0.0251
C	-0.0200	-0.0065	0.0072	-0.0251
D	0.0600	0.0109	-0.0040	0.0058
E	0.0593	0.0393	0.0063	0.0026
F	0.0144	-0.0172	0.0081	-0.0100
G	-0.0170	-0.0056	0.0039	0.0061
H	-0.0254	-0.0179	0.0065	-0.0086
I	-0.0638	0.0195	-0.0284	0.0086
J	0.0747	-0.0182	0.0312	-0.0177
L	-0.0175	0.0170	-0.0316	0.0219
M	0.0277	-0.0221	0.0268	-0.0293
N	-0.0619	0.0119	-0.0316	0.0151
O	-0.0070	-0.0456	-0.0131	-0.0323
P	0.0112	0.0356	-0.0233	0.0182
Q	0.0575	0.0016	0.0163	-0.0044
R	-0.0114	0.0361	-0.0221	0.0296
S	0.0673	-0.0735	0.0710	-0.0168
T	0.0144	0.0296	-0.0198	0.0209
U	0.0428	-0.0591	0.0175	-0.0209

TABLE 3.9.

Atomic x,y and z co-ordinates used in the first cycle of three-dimensional least squares refinement.

ATOM	x/a.	y/b.	z/c.	x(A.U.)	y(A.U.)	z(A.U.)
B	0.1701	0.1647	0.1892	2.403	3.833	0.746
K	-0.1710	0.0770	-0.0486	-2.416	1.791	-0.191
A	0.0957	0.1470	0.1381	1.352	3.421	0.544
C	0.0061	0.1793	0.2716	0.086	4.173	1.070
D	0.0089	0.2339	0.4189	0.125	5.444	1.650
E	0.0952	0.2619	0.4765	1.346	6.095	1.877
F	-0.0827	0.2565	0.4864	-1.168	5.969	1.916
G	-0.1635	0.2323	0.4312	-2.311	5.405	1.699
H	-0.1666	0.1805	0.2815	-2.354	4.200	1.109
I	-0.0784	0.1514	0.1549	-1.107	3.523	0.610
J	-0.0904	0.0960	0.0441	-1.277	2.235	0.174
L	-0.0021	0.0626	-0.1097	-0.029	1.456	-0.432
M	-0.0059	0.0061	-0.2632	-0.084	0.142	-1.037
N	-0.0987	-0.0244	-0.2961	-1.394	-0.567	-1.167
O	-0.0926	-0.0762	-0.4683	-1.308	-1.774	-1.845
P	-0.0075	-0.1052	-0.5679	-0.106	-2.448	-2.238
Q	0.0730	-0.0778	-0.5060	1.031	-1.809	-1.993
R	0.0751	-0.0213	-0.3192	1.060	-0.494	-1.258
S	0.1637	0.0081	-0.2608	2.313	0.188	-1.028
T	0.1691	0.0627	-0.1260	2.390	1.459	-0.496
U	0.0840	0.0876	0.0043	1.187	2.039	0.017

In a Fourier synthesis, the electron density at the atomic peak can be estimated and the corresponding value of B can be read from the graph. This should give a good approximation to the temperature factor provided,

(1) all the observed structure factors are included and the vast majority of the phases are correct,

(2) the observed structure factors are on the correct scale.

In a difference Fourier, provided the co-ordinates are reasonably accurate and the scale factor is within a few percent of the correct value, a good approximation to the temperature factor can be obtained in the following way. The value of $\Delta\rho = \rho_o - \rho_c$ at the atomic position is added to or subtracted from the value of $\rho(0)$ corresponding to the value of the temperature factor assumed for the atom in the structure factor calculation. The new value of $\rho(0)$ is used to obtain the new temperature factor B from the graph.

The values of B obtained from the final Fourier and the final difference Fourier are compared in Table 3,10 and the average values of the individual isotropic temperature factors used in the initial stage of three-dimensional least squares refinement are also shown.

The least squares refinement of the (0kl) zone presents a much more difficult problem. The least squares programme on the Pegasus computer is purely diagonal i.e. it neglects all cross products and in the case of the (0kl) zone, the value of some of the products of the

TABLE 3.10.

Comparison of the temperature factors derived from the final F_o and $(F_o - F_c)$ Fourier syntheses on the (hk0) zone.

ATOM.	B'(A.U.^{2})	B"(A.U.^{2})	Average B.
B	4.4	4.4	4.4
K	4.6	4.6	4.6
A	4.1	4.4	4.2
C	3.7	3.7	3.7
D	4.2	4.6	4.4
E	4.7	5.5	5.1
F	5.1	4.9	5.0
G	4.7	5.0	4.8
H	4.1	4.3	4.2
I	4.2	4.1	4.2
J	4.7	4.7	4.7
L	3.8	3.7	3.8
M	3.8	4.1	3.9
N	4.4	4.7	4.5
O	4.4	4.8	4.6
P	4.8	4.8	4.8
Q	5.0	4.8	4.9
R	3.6	3.6	3.6
S	4.2	4.4	4.3
T	3.9	4.2	4.1
U	4.2	4.0	4.1

B' is the temperature factor derived from the finalF_o Fourier synthesis.

B" is the temperature factor derived from the final $(F_o - F_c)$ Fourier synthesis.

The average value of B quoted was used in the initial stages of three-dimensional least squares refinement.

type $\sum_{q} w \frac{\delta F_c}{\delta z_n} \cdot \frac{\delta F_c}{\delta z_m}$ will be significantly high due to the overlapping in this projection. It was decided, however, to carry out the refinement with the existing programme and to use the y co-ordinates shown in Table 3,9 together with the z co-ordinates in Table 3,5. Only the z co-ordinates were allowed to change and after two cycles it was observed that several of the co-ordinate shifts were oscillating and in these cases a mean was taken between the co-ordinates obtained from the first and second cycles, before carrying out further cycles. The structure factors were recalculated and the reliability index was found to have dropped from 0.20 to 0.18. Three additional cycles of least squares were computed and the reliability index of the structure factors used to compute the last cycle was R = 0.14. The co-ordinate shifts after each cycle are shown in Table 3,11 and by the last cycle the shifts were quite small. On analysing the shifts it was observed that, where two atoms were very close together in this projection, each atom had moved in the same direction and by approximately the same amount. It would appear therefore that the least squares programme neglecting the cross terms, had refined the centres of gravity of the pairs of atoms. The final z co-ordinates are shown in Table 3,9 together with the x and y co-ordinates which were used in the first cycle of three-dimensional least squares refinement.

TABLE 3.11.

z co-ordinate shifts after each cycle of least squares refinement of the (0kl) zone.

ATOM.	CYCLE I.	CYCLE II.	CYCLE III.	CYCLE IV.	CYCLE V.
B	-0.0318	0.0208	-0.1000	0.0777	-0.0144
K	0.0373	-0.0920	0.0552	-0.0580	0.0012
A	-0.1078	0.0768	-0.0698	0.0643	0.0008
C	0.0482	0.0651	-0.0530	0.0461	-0.0007
D	0.0443	0.0703	0.0260	-0.0033	0.0117
E	0.0571	0.0350	-0.0375	0.0294	-0.0085
F	0.0836	0.0372	-0.0304	0.0203	-0.0030
G	0.0534	0.0804	0.0175	0.0007	0.0108
H	0.0544	0.0754	-0.0340	0.0270	0.0033
I	-0.0902	0.0741	-0.0857	0.0740	-0.0026
J	0.1208	0.0287	0.0592	-0.0380	0.0172
L	-0.0074	-0.1536	0.0820	-0.0771	0.0019
M	-0.0591	0.0860	-0.1094	0.0918	-0.0102
N	-0.0030	0.1888	-0.0592	0.0694	0.0085
O	-0.0472	0.0407	0.0546	-0.0379	0.0129
P	0.0741	-0.0678	0.0448	-0.0480	-0.0055
Q	-0.0402	-0.0046	-0.0426	-0.0344	0.0030
R	-0.0257	0.1548	-0.0996	0.0963	0.0020
S	-0.0597	0.0869	-0.1108	0.0919	-0.0114
T	-0.0206	-0.1760	0.0579	-0.0589	-0.0045
U	0.0881	-0.0365	0.0443	-0.0371	0.0028

The co-ordinates used to calculate the structure factors of the third cycle were the average of the co-ordinates derived from Cycle I and Cycle II.

The three-dimensional least squares refinement of 5-methyl 1:2-benzanthraquinone was carried out on the Pegasus computer at the University of Leeds using the least squares programme devised by Dr. D.W.J. Cruickshank. This programme refines 3 positional parameters and six anistropic vibrational parameters for each atom and one overall scale factor for the observed structure factors. In the case of the compound under consideration only the parameters of the carbon and oxygen atoms were allowed to change, the hydrogen contributions to the structure factors remaining the same in each cycle. This meant that 190 parameters were refined.

The anisotropic thermal motion of the carbon and oxygen atoms was obtained by assuming that the stationary scattering factor was multiplied by a term,

$$\exp. -(b_{11}h^2 + b_{22}k^2 + b_{33}l^2 + b_{13}hl + b_{23}kl + b_{12}hk)$$

depending on six parameters b_{ij} different for each atom (Cruickshank, 1956). The programme output is not in the form b_{ij}, but in the form U_{ij}, where U_{ij} are the components of the symmetric tensor describing the anisotropic vibrations of the atoms such that the mean square amplitude of vibration in the direction of the unit vector $\underline{l}$, with components l_i, is

$$\overline{u^2} = \sum_{i=1}^{3}\sum_{j=1}^{3} U_{ij}l_il_j$$

The relationships between the U's and the b's are such that,

$$b_{11} = 2\pi^2.a^{*2}.U_{11}$$

$$b_{12} = 2.2\pi^2 a^* b^* . U_{12}$$

where a^*, b^*, c^* are the reciprocal axes lengths.

The output of the programme gives the new co-ordinates and the new set of U_{ij} values to be used in the next cycle. In addition it also gives the shifts and an estimate of the standard deviations of the co-ordinates used to calculate the structure factors of the cycle and an estimate of the standard deviations of the input U_{ij} terms. It is interesting to note that the standard deviations of the initial z co-ordinates were not significantly higher than those of the x and z co-ordinates, although the z co-ordinates were obtained from the diagonal least squares refinement of the (0kl) zone in which there was no atomic resolution.

Three cycles of least squares were computed using the values of the 635 observed structure factors. The co-ordinate shifts at each stage in the refinement are given in Table 3,12 (a), (b) and (c). The final set of x, y and z co-ordinates are shown in Table 3,13 and the final set of U_{ij} values are given in Table 3,14. The co-ordinates of all the hydrogen atoms, except those of the methyl group, were recalculated using the final carbon and oxygen co-ordinates and assuming a value of 1.05 A.U. for the C - H bond length. The estimated co-ordinates of all the hydrogen atoms are given in Table 3,15.

The reliability indices at each stage in the refinement are shown below,

$$R_{Cycle\ I} = 0.188 \quad R_{Cycle\ II} = 0.171 \quad R_{Cycle\ III} = 0.131$$

At the end of Cycle III the observed structure factors of each individual layer line were scaled to the values of the calculated structure factors. A corrected set of structure factors was thus obtained and on comparing these with the calculated structure factors of Cycle III, it was found that the reliability index dropped to 0.115. The final set of observed and calculated structure factors are given in Table 3,16 along with the values of $\Delta F = F_o - F_c$ and the phase angle α for each reflection. The maximum estimated value of the structure factors of the unobserved reflections are also given in this Table.

TABLE 3.12.

x, y, and z co-ordinate shifts after each cycle of three-dimensional least squares refinement. (Values in A.U.)

(a) x co-ordinate shifts.

ATOM	CYCLE I	CYCLE II	CYCLE III
B	0.0088	0.0035	0.0139
K	-0.0058	0.0148	-0.0165
A	-0.0700	0.0478	-0.0435
C	0.0249	-0.0231	0.0007
D	0.0165	-0.0292	0.0024
E	0.0324	0.0160	0.0061
F	0.0348	0.0430	-0.0085
G	-0.0084	0.0209	-0.0217
H	0.0036	-0.0121	0.0238
I	-0.0325	0.0056	-0.0130
J	0.0297	-0.0572	0.0160
L	-0.0264	-0.0249	0.0244
M	-0.0429	0.0137	-0.0080
N	0.0390	-0.0404	0.0268
O	-0.0112	0.0037	0.0167
P	0.0000*	-0.0043	0.0179
Q	0.0000	0.0084	0.0195
R	0.0000	-0.0041	0.0278
S	0.0000	-0.0034	-0.0138
T	0.0000	-0.0370	-0.0044
U	0.0000	0.0018	-0.0247

* In the first cycle Pegasus failed to solve the least squares equations for atoms P to U.

TABLE 3.12.

(b) y co-ordinate shifts.

ATOM	CYCLE I	CYCLE II	CYCLE III
B	0.0258	-0.0002	0.0030
K	-0.0115	0.0055	-0.0019
A	-0.0239	-0.0005	-0.0040
C	-0.0244	0.0063	-0.0113
D	-0.0100	-0.0281	0.0174
E	-0.0054	0.0029	-0.0213
F	0.0167	0.0072	-0.0065
G	-0.0064	-0.0028	0.0063
H	-0.0160	-0.0021	0.0073
I	-0.0015	0.0044	0.0043
J	-0.0039	0.0063	-0.0313
L	-0.0260	0.0015	0.0104
M	-0.0350	0.0307	-0.0241
N	-0.0403	-0.0246	0.0131
O	-0.0092	-0.0207	-0.0094
P	0.0000*	-0.0145	0.0095
Q	0.0000	0.0356	0.0057
R	0.0000	0.0126	0.0278
S	0.0000	0.0016	-0.0189
T	0.0000	-0.0068	-0.0146
U	0.0000	0.0097	-0.0090

TABLE 3.12.

(c) z co-ordinate shifts.

ATOM	CYCLE I	CYCLE II	CYCLE III
B	-0.0223	-0.0444	0.0256
K	-0.0117	0.0088	-0.0187
A	0.0138	-0.0356	0.0057
C	-0.0610	0.0204	-0.0479
D	-0.0240	0.0031	-0.0130
E	-0.0015	-0.0274	0.0128
F	0.0327	0.0052	-0.0088
G	0.0181	-0.0099	0.0175
H	0.0059	0.0074	-0.0438
I	0.0990	-0.0168	0.0159
J	-0.0700	-0.0186	-0.0017
L	0.1324	-0.0339	0.0479
M	0.0568	-0.0013	0.0305
N	0.0367	0.0562	-0.0103
O	0.0000	0.1170	0.0143
P	0.0000*	0.0644	0.0128
Q	0.0000	0.0039	0.0046
R	0.0000	-0.0709	0.0345
S	0.0000	-0.0881	-0.0104
T	0.0000	-0.0659	0.0169
U	0.0000	-0.0723	0.0097

TABLE 3.13.

The final carbon and oxygen atomic co-ordinates.

ATOM	x (A.U.)	y (A.U.)	z (A.U.)
B	2.4290	3.8614	0.7045
K	-2.4237	1.7830	-0.2130
A	1.2867	3.3925	0.5279
C	0.0890	4.1431	0.9816
D	0.1152	5.4229	1.6163
E	1.4002	6.0711	1.8611
F	-1.0991	5.9866	1.9456
G	-2.3199	5.4018	1.7247
H	-2.3388	4.1897	1.0785
I	-1.1473	3.5301	0.7083
J	-1.2883	2.2060	0.0833
L	-0.0560	1.4417	-0.2857
M	-0.1207	0.1128	-0.9508
N	-1.3691	-0.6191	-1.0842
O	-1.2992	-1.8134	-1.7138
P	-0.0924	-2.4532	-2.1605
Q	1.0594	-1.7679	-1.9849
R	1.0842	-0.4541	-1.2941
S	2.2955	0.1703	-1.1261
T	2.3486	1.4372	-0.5454
U	1.1644	2.0396	-0.0457

TABLE 3.14.

The values of U_{ij} derived from the last cycle of three - dimensional least squares refinement.

(The values in 10^{-2} A.U.^{2})

ATOM	U_{11}	U_{22}	U_{33}	U_{12}	U_{23}	U_{13}
B	4.62	5.74	13.67	-2.59	-4.46	-2.27
K	4.81	5.19	18.88	-0.17	-7.10	-2.61
A	2.70	5.74	8.44	-0.31	4.37	-3.92
C	5.13	3.96	8.38	-0.36	3.44	-2.37
D	7.13	5.78	6.02	2.48	3.35	0.02
E	8.78	5.37	10.34	0.31	-1.89	5.87
F	8.30	4.60	6.75	-0.85	-0.93	0.75
G	7.35	7.48	4.14	1.74	1.79	2.73
H	4.34	8.24	8.57	0.03	0.71	7.07
I	4.50	5.92	8.48	0.82	7.01	-0.95
J	4.26	5.57	10.70	-2.55	4.68	-2.33
L	5.01	3.79	6.06	0.95	1.28	-1.99
M	5.86	4.11	6.04	0.82	0.68	0.92
N	5.66	6.93	8.35	-0.98	0.26	-3.73
O	6.96	6.08	9.16	-2.25	-1.83	-0.45
P	8.95	5.15	7.39	-0.45	1.26	-6.03
Q	7.76	6.16	7.45	2.84	-0.45	-1.01
R	5.27	5.00	6.26	1.30	1.05	-2.23
S	3.94	6.15	7.75	2.99	-0.24	0.10
T	5.54	4.54	9.27	0.95	2.43	1.93
U	3.49	5.85	6.94	0.14	4.48	2.63

TABLE 3.15.

The calculated hydrogen atomic co-ordinates.

ATOM	x (A.U.)	y (A.U.)	z (A.U.)
F'	-1.0801	6.9245	2.4180
G'	-3.2168	5.8705	2.0014
H'	-3.2591	3.7273	0.8768
N'	-2.2677	-0.1929	-0.7500
O'	-2.1994	-2.3268	-1.8723
P'	-0.0819	-3.4019	-2.6077
Q'	1.9584	-2.1918	-2.3191
S'	3.1773	-0.4768	-1.4413
T'	3.2648	1.9286	-0.3949
E_1'	1.6425	6.2508	2.8072
E_2'	2.0181	5.4596	1.5227
E_3'	1.2327	6.9954	1.4952

TABLE 3,16.

THE OBSERVED AND CALCULATED STRUCTURE FACTORS OF 5-METHYL 1:2-BENZANTHRAQUINONE.

h	k	l	F_o	F_c	ΔF	α°	h	k	l	F_o	F_c	ΔF	α°	h	k	l	F_o	F_c	ΔF	α°
0	2	0	36.8	34.3	2.5	0.0	4	6	0	42.4	39.5	2.9	297.0	8	6	0	13.4	13.7	-0.3	[illegible]
	4		30.5	30.2	0.3	0.0		8		12.6	12.4	0.2	276.0		8		9.0	9.5	-0.5	100.3
	6		53.9	51.0	2.9	180.0		10		18.5	17.5	1.0	43.0		10		7.6	7.6	0.0	326.0
	10		9.5	10.0	-0.5	180.0		12		19.5	18.5	1.0	180.6		12		10.2	11.6	-1.4	173.5
	12		105.5	98.2	7.3	0.0		14		8.0	9.7	-1.7	167.5		14		8.3	8.9	-0.6	226.3
	14		12.8	12.8	0.0	0.0		16		16.1	16.3	-0.2	359.2		16		10.0	7.8	2.2	348.8
	16		5.9	0.7	5.2	0.0		18		22.2	24.0	-1.8	317.4		18		10.9	12.0	-1.1	26.6
	18		3.8	2.9	0.9	180.0		20		11.8	14.1	-2.3	279.2		20		6.6	6.1	0.5	33.8
	20		7.1	8.8	-1.7	180.0		22		7.1	7.0	0.1	49.7		22		4.7	6.3	-1.6	325.9
	22		2.2	0.6	1.6	180.0		24		3.2	2.9	0.3	212.8		24		4.4	3.8	0.6	160.0
	24		6.6	7.6	-1.0	180.0		26		2.8	3.5	-0.7	250.8		26		2.5	2.3	0.2	247.8
1	2	0	77.1	76.5	0.6	91.7		28		2.1	1.6	0.5	6.2	9	2	0	15.8	16.7	-0.9	247.0
	4		54.2	50.2	4.0	256.6	5	2	0	33.9	28.7	5.2	82.7		4		3.6	4.0	-0.4	277.6
	6		7.7	6.9	0.8	357.9		4		14.8	13.4	1.4	53.5		6		6.0	5.4	0.6	260.3
	8		46.9	41.3	5.6	161.5		6		97.4	89.1	8.3	89.2		8		2.4	1.2	1.2	303.3
	10		49.2	42.0	7.2	275.6		8		46.1	40.2	5.9	8.4		10		8.0	9.0	-1.0	105.8
	12		29.8	24.6	5.2	269.6		10		10.0	10.1	-0.1	271.6		14		6.0	5.2	0.8	251.3
	14		8.7	7.9	0.8	64.6		12		12.3	12.2	0.1	283.5		16		2.3	2.2	0.1	15.8
	16		6.4	5.9	0.5	241.9		14		16.1	13.5	2.6	90.7		18		3.5	3.5	0.0	232.4
	18		5.6	4.9	0.7	5.4		16		6.5	6.8	-0.3	288.8		20		3.6	4.2	-0.6	236.3
	20		8.8	9.0	-0.2	166.9		18		36.6	39.9	-3.3	94.9		22		2.9	4.0	-1.1	123.3
	22		5.2	8.0	-2.8	96.6		20		17.0	16.1	0.9	14.4		24		2.6	3.7	-1.1	83.6
	24		11.3	12.8	-1.5	99.2		22		5.7	5.5	0.2	303.7	10	0	0	32.4	32.8	-0.4	309.4
	26		1.8	1.9	-0.1	183.9		24		4.0	4.6	-0.6	347.8		2		20.0	23.9	-3.9	275.7
	28		2.4	2.6	-0.2	32.9		26		2.2	1.3	0.9	71.7		4		4.8	3.8	1.0	193.4
2	0	0	119.0	122.7	-3.7	359.7		28		2.0	1.9	0.1	222.5		6		15.4	14.1	1.3	200.4
	2		24.5	22.8	1.7	51.8	6	0	0	31.5	30.4	1.1	3.5		8		4.9	4.4	0.5	342.7
	4		13.6	10.8	2.8	44.5		2		12.7	13.1	-0.4	109.1		12		4.4	5.0	-0.6	355.9
	6		45.2	46.2	0.0	123.5		4		16.5	14.7	1.8	1.3		14		4.6	4.9	-0.3	271.9
	8		24.6	26.5	-1.9	20.4		6		26.7	25.0	1.7	4.9		16		4.9	3.3	1.6	180.3
	10		12.5	11.0	1.5	315.6		8		32.1	28.7	3.4	199.8		18		4.9	6.0	-1.1	246.5
	12		11.5	9.8	1.7	13.0		10		10.1	9.9	0.2	31.8		20		2.6	2.1	0.5	319.0
	14		13.1	10.3	2.8	112.5		12		9.9	9.9	0.0	1.3		22		3.4	3.6	-0.2	67.6
	16		6.1	4.4	1.7	98.5		14		4.5	4.7	-0.2	267.0		24		3.6	3.8	-0.2	183.3
	18		10.4	9.8	0.6	107.0		16		25.4	26.5	-1.1	347.9	11	2	0	25.6	26.2	-0.6	108.0
	20		4.4	4.2	0.2	35.5		18		33.7	32.8	0.9	353.3		4		5.6	6.8	-1.2	288.1
	22		3.3	3.6	-0.3	332.4		20		9.0	9.8	-0.8	223.6		6		2.3	2.2	0.1	176.6
	24		6.1	6.4	-0.3	184.1		22		4.1	4.9	-0.8	342.3		8		3.4	4.0	-0.6	80.4
	26		2.4	3.9	-1.5	262.3		28		2.2	2.4	-0.2	339.1		10		13.2	13.5	-0.3	265.9
	28		1.7	3.0	-1.3	298.9	7	2	0	10.7	14.7	-4.0	67.5		12		5.8	7.3	-1.5	255.7
3	2	0	70.8	66.5	4.3	267.4		4		20.0	20.5	-0.5	19.6		14		6.2	7.6	-1.4	129.8
	4		8.0	8.0	0.0	239.0		6		63.0	56.2	6.8	82.8		16		1.8	3.6	-1.8	180.8
	6		11.0	10.4	0.6	270.6		8		12.1	9.6	2.5	102.6		20		4.3	4.9	-0.6	6.0
	10		26.6	25.6	1.0	83.6		10		6.3	6.0	0.3	261.6		22		4.0	4.2	0.2	44.6
	12		2.8	1.9	0.9	3.9		12		6.6	7.4	-0.8	243.7	12	0	0	66.4	62.6	3.8	338.9
	14		13.9	14.4	-0.5	285.0		14		8.0	9.0	-1.0	100.5		2		19.3	21.9	-2.6	208.1
	16		2.3	3.9	-1.6	217.2		16		13.2	15.1	-1.9	358.2		4		3.2	2.6	0.6	180.8
	18		2.7	1.1	1.6	246.1		18		29.2	30.9	-1.7	86.6		6		3.0	3.3	-0.3	111.6
	20		8.0	9.6	-1.6	322.4		20		9.4	10.0	-0.6	161.2		8		7.2	6.9	0.3	108.6
	22		5.1	5.4	-0.3	35.1		22		6.2	7.0	-0.8	189.2		10		9.3	10.4	-1.1	360.6
	24		1.8	3.7	-1.9	79.5		26		2.9	2.5	0.4	161.9		12		17.5	21.1	-3.6	0.8
4	0	0	69.3	67.8	1.5	178.3	8	0	0	15.9	13.5	2.4	181.3		14		6.4	5.9	0.5	359.2
	2		18.4	16.1	2.3	256.0		2		5.8	6.5	-0.7	138.0		20		2.3	3.6	-1.3	152.8
	4		4.5	5.6	-1.1	29.7		4		10.8	11.0	0.2	15.7	13	2	0	11.2	13.4	-2.2	180.0

h	k	l	Fo	Fc	ΔF	α°
13	4	0	4.4	3.7	0.7	275.1
	6		2.9	4.2	−1.3	83.7
	8		9.2	8.3	0.9	169.9
	10		5.3	5.5	−0.2	260.2
	12		4.2	4.7	−0.5	92.4
	16		2.3	3.0	−0.7	227.5
	18		2.2	2.5	−0.3	83.9
	20		2.0	0.8	1.2	180.0
14	0	0	3.5	4.3	−0.8	4.3
	2		1.9	2.1	−0.2	222.6
	4		3.0	4.0	−1.0	11.9
	6		3.6	4.9	−1.3	106.8
	8		2.3	4.0	−1.7	30.8
	10		2.3	2.7	−0.4	315.2
	14		2.3	1.4	0.9	99.3
	16		1.8	1.5	0.3	39.3
	18		2.0	1.0	1.0	55.0
15	2	0	8.3	8.0	0.3	258.3
	8		4.6	5.9	−1.3	347.2
	10		3.2	3.6	−0.4	68.0
	14		3.1	3.0	0.1	261.9
16	0	0	7.5	5.3	2.2	173.8
	4		2.4	2.7	−0.3	15.2
	6		4.9	4.3	0.6	270.8
	8		4.2	3.3	0.9	245.8
	10		4.7	3.9	0.8	79.6
17	2	0	1.8	2.7	−0.9	44.4
	4		3.9	3.8	0.1	4.1
	6		8.1	6.5	1.6	80.8
	8		8.3	7.0	1.3	7.0
	10		2.7	3.2	−0.5	294.6
18	0	0	3.8	5.3	−1.5	87.8
	4		2.6	3.0	−0.4	24.4
0	1	1	26.7	27.9	−1.2	0.0
	2		59.6	59.3	0.3	180.0
	3		26.1	25.2	0.9	180.0
	4		89.3	83.5	5.8	0.0
	5		25.7	29.0	−3.3	180.0
	6		8.7	7.7	1.0	180.0
	7		11.6	10.7	0.9	180.0
	8		54.1	46.2	7.9	180.0
	9		38.8	32.8	6.0	180.0
	12		9.0	9.0	0.0	180.0
	13		16.7	15.6	1.1	0.0
	14		25.5	24.0	1.5	180.0
	15		6.0	4.5	1.5	0.0
	16		10.7	12.3	−1.5	0.0
	17		3.9	5.6	−1.7	180.0
	19		2.9	5.1	−2.2	0.0
	20		6.4	5.1	1.3	0.0
	21		6.2	8.5	−2.3	0.0
	22		5.8	6.7	−0.9	0.0
	24		3.3	2.7	0.6	0.0
	26		5.9	5.6	0.3	0.0
	27		6.0	5.4	0.6	180.0
1	0	1	17.1	16.8	0.3	19.7
	1		20.1	23.4	−3.3	149.5
	2		95.0	109.0	−14.0	274.7
	3		142.5	158.4	−15.9	82.8
	4		65.3	68.0	−2.7	289.5
	5		11.5	11.6	−2.1	282.3
	6		20.0	12.5	7.5	68.8

h	k	l	Fo	Fc	ΔF	α°
1	7	1	17.4	13.3	4.1	134.9
	8		14.5	13.7	0.8	287.0
	9		52.2	50.3	1.9	254.9
	10		30.1	22.6	7.5	289.3
	11		9.1	8.6	0.5	306.8
	12		3.0	3.5	−0.5	115.5
	13		3.9	2.2	1.7	220.5
	14		15.3	15.5	−0.2	279.8
	15		25.0	23.9	1.1	79.5
	16		14.3	14.6	−0.3	318.9
	18		6.6	7.3	−0.7	49.1
	19		5.1	3.1	2.0	187.7
	22		4.9	5.7	−0.8	77.0
	24		5.7	5.7	0.0	216.7
2	1	1	14.3	17.8	−2.5	195.1
	2		17.8	17.8	0.0	119.2
	3		22.8	25.2	−2.4	267.7
	4		13.7	12.2	1.5	104.2
	5		18.7	17.0	1.7	45.0
	6		22.4	21.8	0.6	111.3
	7		8.9	9.4	−0.5	346.8
	8		5.8	8.5	−2.7	222.4
	9		4.4	6.2	−1.6	259.0
	10		7.8	7.5	0.3	150.4
	11		15.3	16.8	−1.5	225.2
	12		3.3	3.2	0.1	102.7
	13		3.4	3.3	0.1	110.2
	14		7.2	4.8	2.4	209.6
	15		8.4	6.4	2.0	276.3
	16		4.8	3.2	1.6	187.0
	17		6.1	6.0	0.1	94.8
	18		4.4	4.4	0.0	117.3
	19		4.4	4.6	−0.2	353.3
	20		5.5	4.8	0.7	357.6
	21		7.3	8.1	−0.8	11.2
3	0	1	10.5	13.4	−2.9	176.3
	1		3.8	3.5	0.3	279.0
	2		18.4	20.1	−1.7	97.0
	3		13.6	14.4	−0.8	253.2
	4		6.8	8.2	−1.4	126.5
	5		3.2	2.7	0.5	164.7
	6		24.2	22.8	1.4	281.5
	7		10.0	9.5	0.5	239.9
	9		13.5	13.4	0.1	99.5
	10		6.0	7.1	−1.1	102.9
	11		15.8	16.6	−0.8	78.4
	12		5.6	5.6	0.0	288.9
	15		8.2	9.9	−1.7	237.1
	17		9.3	9.9	−0.6	214.2
	18		5.9	5.2	0.7	307.3
	21		4.5	4.9	−0.4	75.1
4	1	1	8.9	12.3	−3.4	189.9
	2		19.0	21.6	−2.6	17.2
	3		28.5	31.0	−2.5	16.4
	4		8.7	8.5	0.2	310.4
	5		21.8	22.5	−0.7	299.5
	6		17.5	17.8	−0.3	251.5
	8		20.0	16.9	3.1	357.7
	9		18.0	17.9	0.1	174.8
	10		14.5	12.8	1.7	307.4
	11		10.6	8.7	1.9	96.4
	12		4.9	5.0	−0.1	294.9

h	k	l	Fo	Fc	ΔF	α°
4	13	1	4.4	4.5	−0.1	185.4
	14		8.2	10.4	−2.2	[illegible]
	15		17.3	16.4	0.9	29.9
	16		8.2	6.5	1.7	336.9
	17		10.0	9.5	0.5	187.0
	18		11.6	12.7	−1.1	200.8
	21		9.2	8.7	0.6	186.9
	22		9.1	6.9	2.2	295.2
	23		5.6	4.9	0.7	70.7
	24		6.5	5.7	0.8	245.8
5	0	1	16.0	13.1	2.9	123.0
	1		4.1	7.4	−3.3	331.1
	2		21.4	20.9	0.5	265.7
	3		20.0	22.0	−2.0	227.1
	4		19.8	19.1	0.7	168.2
	5		14.6	17.3	−2.7	148.9
	6		4.3	5.8	−1.5	52.5
	7		11.3	8.7	2.5	17.3
	8		15.3	15.6	−0.3	266.6
	9		8.0	8.8	−0.8	29.6
	10		8.0	8.9	−0.9	146.7
	11		7.6	7.0	0.6	283.3
	13		6.4	6.4	0.0	232.4
	14		23.4	24.4	−1.0	264.4
	15		21.0	22.2	−1.2	247.1
	16		14.5	15.4	−0.9	207.8
	17		9.2	10.3	−1.1	187.1
	18		5.9	7.1	−1.2	218.6
	19		9.8	7.9	1.9	69.8
	20		15.7	15.3	0.4	262.0
	21		10.0	8.6	1.4	75.4
	22		5.5	5.9	−0.4	168.3
	23		5.8	6.1	−0.3	315.3
6	1	1	14.2	13.8	0.4	330.8
	2		13.5	12.1	1.4	340.0
	3		32.6	32.4	0.2	0.0
	4		50.5	50.2	0.3	354.3
	5		8.3	8.0	0.3	207.4
	6		9.6	10.4	−0.8	262.1
	7		11.9	13.2	−1.3	149.9
	8		13.3	14.1	−0.8	340.3
	9		44.2	41.3	2.9	176.5
	10		20.9	18.1	1.2	350.7
	11		12.6	12.3	0.3	29.6
	12		5.4	4.7	0.7	251.9
	13		7.2	9.4	−2.2	176.9
	14		5.3	5.2	0.1	318.4
	15		23.3	24.6	−1.3	356.1
	16		24.4	22.8	1.6	0.7
	18		4.8	5.5	−0.7	232.7
	19		6.0	6.3	−0.3	98.9
	20		7.4	8.7	−1.3	354.4
	21		31.0	30.3	0.7	198.3
	22		10.8	10.1	0.7	4.7
7	0	1	8.6	10.6	−2.0	3.8
	1		11.2	9.9	1.3	283.7
	2		19.5	21.6	−2.1	300.1
	3		14.5	15.2	−0.7	333.1
	4		10.8	10.2	0.6	8.4
	8		11.1	8.7	2.4	271.3
	9		4.4	3.8	0.6	188.7
	10		6.2	5.3	0.9	63.6

h	k	l	F_o	F_c	ΔF	α°
7	11	1	3.0	2.8	0.2	309.5
	12		7.8	6.4	1.4	203.7
	13		7.7	6.5	1.2	264.6
	14		18.1	20.1	-2.0	277.5
	15		17.0	17.6	-0.6	285.7
	16		5.6	6.0	-0.4	287.0
	17		5.9	5.9	0.0	332.4
	18		6.4	6.4	0.0	216.9
	19		6.0	4.8	1.2	122.5
	20		14.1	12.1	2.0	268.2
	21		9.5	7.9	1.6	89.2
8	1	1	5.4	5.9	-0.5	225.0
	2		8.8	9.6	-0.8	320.5
	3		12.5	13.3	-0.8	338.9
	5		9.7	9.2	0.5	52.5
	7		6.3	6.5	-0.2	66.5
	8		10.1	10.8	-0.7	357.3
	9		6.1	5.7	0.4	156.7
	10		7.4	5.7	1.7	60.0
	13		8.0	7.7	0.3	245.5
	14		7.3	6.8	0.5	202.1
	15		8.7	9.1	-0.4	315.7
	19		5.6	5.4	0.2	83.6
	20		5.9	5.3	0.6	17.9
9	0	1	4.3	5.6	-1.3	175.5
	1		5.5	6.7	-1.2	340.6
	5		5.5	6.3	-0.8	307.7
	6		9.9	9.5	0.4	253.9
	9		5.9	4.5	1.4	50.0
	11		8.2	6.8	1.4	101.9
	12		3.9	3.2	0.7	210.1
	21		5.1	3.8	1.3	70.1
10	2	1	8.0	8.8	-0.8	266.2
	3		6.2	6.3	-0.1	125.7
	6		6.0	5.1	0.9	255.2
	8		5.7	5.3	0.4	164.8
	21		5.7	4.7	1.0	338.5
11	0	1	17.2	22.5	-5.3	162.1
	1		16.5	14.2	2.3	30.7
	2		20.7	22.3	-1.6	246.1
	3		28.0	28.8	-0.8	96.5
	4		15.5	16.4	-0.9	235.5
	5		10.7	10.1	0.6	0.6
	6		10.9	9.9	1.0	136.1
	9		10.3	10.6	-0.3	272.3
	10		6.9	6.5	0.4	250.3
	11		7.9	7.1	0.8	242.0
	14		4.8	5.4	-0.6	240.8
	15		9.1	8.8	0.3	112.3
	16		5.9	4.8	1.1	234.0
12	1	1	9.1	8.1	1.0	26.9
	2		10.3	9.8	0.5	202.3
	4		17.1	19.1	-2.0	18.4
	5		10.6	9.3	1.3	184.1
	7		5.8	4.5	1.3	140.8
	8		10.4	9.3	1.1	203.1
	9		8.6	8.3	0.3	181.1
	13		6.3	5.0	1.3	12.0
	14		7.0	5.4	1.6	151.0
13	0	1	7.0	8.1	-1.1	176.1
	2		14.0	13.7	0.7	265.4
	3		16.8	15.9	0.9	76.3

h	k	l	F_o	F_c	ΔF	α°
13	4	1	9.3	8.4	0.9	283.0
	5		7.7	7.7	0.0	2.8
	7		6.8	5.1	1.7	164.4
	9		7.5	6.7	0.8	239.1
	10		5.3	4.7	0.6	298.0
0	0	2	16.6	16.6	0.0	0.0
	1		7.5	10.2	-2.7	0.0
	2		16.5	22.0	-5.5	180.0
	3		14.8	5.2	9.6	180.0
	4		15.3	12.7	2.6	180.0
	5		66.8	62.1	4.7	0.0
	6		108.0	105.6	2.4	180.0
	7		4.5	1.5	3.0	180.0
	9		14.5	14.5	0.0	180.0
	12		9.0	8.8	0.2	0.0
	17		13.0	11.9	1.1	0.0
	18		12.7	12.4	0.3	180.0
	19		10.9	11.5	-0.6	0.0
	21		7.4	8.3	-0.9	180.0
1	1	2	4.7	8.0	-3.3	154.3
	2		14.9	14.6	0.3	292.7
	3		7.6	11.3	-3.7	339.4
	4		26.5	27.0	-0.5	65.8
	5		18.4	20.5	-2.1	152.9
	6		8.7	7.4	1.3	16.9
	7		35.5	36.7	-1.2	103.9
	8		8.7	8.6	0.1	288.9
	9		7.9	4.9	3.0	206.4
	10		12.9	11.3	1.6	65.8
	11		4.4	4.0	0.4	161.2
	13		5.8	6.2	-0.4	170.3
	14		6.5	6.7	-0.2	249.2
	15		6.8	7.3	-0.5	324.3
	16		8.0	5.3	2.7	79.6
	17		14.0	13.7	0.3	264.4
	18		7.6	9.4	-1.8	287.7
2	0	2	17.8	17.6	0.2	335.4
	1		11.4	13.0	-1.6	274.1
	2		4.9	6.2	-1.3	181.0
	3		3.7	7.7	-4.0	167.1
	4		12.3	11.9	0.4	222.9
	5		16.8	16.8	0.0	31.5
	6		33.9	30.6	3.3	164.5
	7		7.7	9.4	-1.7	359.7
	8		10.0	8.5	1.5	270.8
	9		4.8	3.4	1.4	79.1
	10		4.6	2.4	2.2	176.2
	11		5.8	7.2	-1.4	93.1
	12		5.7	5.5	0.2	306.0
	13		6.0	5.7	0.3	299.5
	14		4.2	4.3	-0.1	212.5
	19		5.7	5.7	0.0	15.0
3	1	2	5.8	7.7	-1.9	261.3
	2		4.5	5.6	-1.1	254.5
	3		6.2	8.0	-1.8	117.2
	4		8.5	8.8	-0.3	299.3
	5		13.1	11.8	1.3	197.4
	6		8.2	6.0	2.2	42.1
	7		14.1	10.7	3.4	234.6
	8		11.0	12.8	-1.8	89.6
	9		4.5	3.1	1.4	216.2
	11		5.6	4.9	0.7	332.0

h	k	l	F_o	F_c	ΔF	α°
3	22	2	5.8	6.3	-0.5	304.8
4	0	2	22.2	22.3	-0.1	116.4
	1		13.9	18.3	-4.4	97.2
	2		13.2	15.4	-2.2	44.6
	3		10.0	9.5	0.5	252.8
	4		5.0	4.4	0.6	143.3
	5		6.7	10.0	-3.3	190.1
	6		10.6	11.0	-0.4	358.6
	7		4.2	6.0	-1.8	85.0
	9		9.8	7.5	2.3	30.1
	10		6.6	6.6	0.0	197.3
	11		4.6	5.5	-0.9	164.2
	12		15.0	17.0	-2.0	102.5
	13		13.7	13.8	-0.1	115.5
	14		11.4	12.9	-1.5	100.2
	15		5.4	6.0	-0.6	90.1
	16		6.3	5.1	1.2	212.7
	22		8.5	6.2	2.3	185.8
	24		5.9	4.5	1.4	138.0
5	1	2	26.1	28.0	-1.9	278.5
	2		11.9	14.5	-2.6	231.8
	3		12.2	16.5	-4.3	156.7
	4		3.8	6.1	-2.3	171.9
	5		5.3	5.4	-0.1	44.0
	7		7.8	7.2	0.6	43.0
	8		9.5	9.0	0.5	275.2
	10		8.2	7.7	0.5	189.4
	11		11.8	11.8	0.0	65.4
	12		29.8	31.8	-2.0	276.6
	13		14.0	11.1	2.9	306.2
	14		11.6	11.5	0.1	199.8
	15		6.6	7.3	-0.7	170.6
	23		8.2	8.2	0.0	67.9
	24		11.6	11.0	0.6	281.4
	25		5.5	5.5	0.0	57.4
6	0	2	28.6	27.1	1.5	193.7
	1		14.0	16.2	-2.2	75.2
	10		13.3	13.2	0.1	167.5
	11		12.3	15.0	2.7	188.5
	12		22.5	21.9	0.6	174.9
	13		16.8	17.6	-0.8	170.0
	14		4.8	5.3	-0.5	88.1
	16		7.3	9.0	-1.7	167.9
	22		10.9	8.5	2.4	170.8
	23		7.0	6.4	0.6	2.1
	24		8.4	6.1	2.3	169.7
	25		4.9	6.3	-1.4	186.6
7	1	2	20.9	20.1	-0.8	257.3
	2		7.2	7.2	0.0	301.9
	8		6.3	5.4	0.9	93.4
	10		5.5	7.9	-2.4	180.8
	11		12.3	10.9	1.4	129.2
	12		24.0	25.0	-1.0	249.1
	13		7.2	6.7	0.5	208.9
	23		7.3	7.2	0.1	110.7
	24		9.5	8.9	0.6	269.0
8	0	2	13.4	17.3	-3.9	258.4
	1		6.3	6.7	-0.4	312.8
	3		6.3	7.2	-0.9	181.9
	10		7.2	6.0	1.2	165.3
	13		8.3	7.7	0.6	284.9
9	5	2	7.4	7.7	-0.3	[illegible]

h	k	l	Fo	Fc	ΔF	α°
9	7	2	6.4	6.9	−0.5	305.2
10	2	2	7.0	9.2	−2.2	236.6
	4		12.1	12.6	−0.5	104.5
	5		10.2	9.8	−0.4	335.6
	6		16.9	12.3	2.6	180.3
	8		10.4	8.8	1.6	91.4
11	4	2	11.7	12.2	−0.5	109.6
	5		6.6	7.9	−1.3	21.0
	7		15.0	12.1	2.9	65.8
	8		8.3	8.3	0.0	293.3
12	3	2	7.8	6.7	1.1	269.1
	4		11.7	10.7	1.0	104.9
	5		17.1	15.1	2.0	4.6
	6		25.4	24.1	1.3	178.6
	8		8.1	6.3	1.8	96.4
13	7	2	11.1	10.8	0.3	110.5
0	2	3	10.9	11.3	−0.4	0.0
	3		11.7	14.3	−2.6	0.0
	4		4.3	6.7	−2.4	0.0
	5		6.7	8.8	−2.1	0.0
	7		3.9	6.6	−2.7	180.0
	8		6.6	5.0	1.6	0.0
	9		13.4	16.4	−3.0	0.0
	10		17.4	19.2	−2.0	180.0
	11		5.0	9.2	−4.2	0.0
	12		5.0	5.1	−0.1	0.0
	13		3.1	5.1	−2.0	180.0
	14		4.2	5.6	−1.4	180.0
	15		5.8	6.9	−1.1	180.0
	16		3.5	3.4	0.1	180.0
	19		7.7	8.6	−0.9	180.0
	20		2.5	2.1	0.4	0.0
	21		2.8	3.7	−0.9	0.0
	22		3.1	6.4	−3.3	180.0
1	1	3	6.6	9.2	−2.6	286.3
	3		11.0	15.3	−3.3	77.7
	4		14.3	14.7	−0.4	73.6
	6		6.3	7.0	−0.7	187.5
	7		10.8	8.8	2.0	227.3
	8		23.0	26.7	−3.7	86.5
	9		21.2	25.8	−4.6	263.6
	10		9.6	6.0	3.6	118.5
	11		5.8	9.6	−3.8	97.7
	12		5.6	4.4	1.2	219.4
2	2	3	4.0	6.1	−1.9	308.4
	3		6.9	8.0	−1.1	67.6
	4		4.1	2.8	1.3	69.2
	5		5.8	6.2	−0.4	85.6
	7		7.2	8.1	−0.9	127.3
	8		11.0	13.4	−2.4	270.8
	9		8.3	8.5	−0.2	76.9
	10		5.3	4.8	0.5	161.8
	12		5.6	7.5	−1.9	286.2
3	1	3	7.3	7.6	−0.3	110.4
	2		4.6	7.0	−2.4	25.4
	4		4.4	5.5	−1.1	305.8
	10		5.7	7.4	−1.7	48.1
	11		6.9	8.4	−1.5	316.8
4	1	3	6.3	8.5	−2.2	112.6
	2		7.1	8.9	−1.8	14.0
	3		6.6	7.0	−0.4	216.2
	9		9.2	11.1	−1.9	217.8
	10		10.2	7.4	2.8	226.6
	11		7.2	6.8	0.4	153.4
	12		7.0	7.3	−0.3	78.0
	14		4.8	5.0	−0.2	185.3
	15		5.7	5.2	0.5	353.3
5	1	3	8.2	11.6	3.4	138.3
5	2	3	5.5	8.7	−3.2	10.8
	3		8.7	9.1	−0.4	260.9
	4		5.4	8.7	−3.3	110.3
	6		7.7	7.3	0.4	297.6
	8		10.2	11.2	−1.0	97.9
	9		13.6	16.5	−2.9	78.1
	10		8.8	11.6	−2.8	86.7
	11		6.8	10.6	−3.7	11.9
6	1	3	7.8	5.0	2.8	100.3
	2		10.4	11.0	−0.6	11.1
	3		5.6	6.4	−0.8	188.1
	9		7.2	6.5	0.7	178.6
	10		10.3	10.4	−0.1	176.8
	14		8.6	10.6	−2.0	170.0
	15		9.7	10.6	−0.9	180.7
7	3	3	8.0	9.7	−1.7	311.5
	4		6.3	8.7	−1.4	116.5
	8		9.2	11.3	−2.1	91.4
	9		10.6	14.0	−3.4	110.3
0	0	4	8.5	11.1	−2.6	0.0
	1		7.0	9.3	−2.3	0.0
	10		6.6	6.0	0.6	0.0
	11		10.1	12.6	−2.5	180.0
	12		8.3	12.5	−4.2	0.0
	14		5.4	8.9	−3.5	180.0
	15		3.2	5.8	−2.6	0.0
1	1	4	7.2	9.1	−1.9	282.6
	10		6.5	7.1	−1.6	233.8
	11		5.7	7.3	−1.6	23.0
	12		9.1	12.2	−3.1	102.0
2	9	4	4.0	3.1	0.9	268.0
	10		5.6	4.9	0.7	57.9
	11		4.7	7.7	−3.0	161.7

h	k	l	Fo
0	8	0	< 1.0
	26		< 1.5
	28		< 1.2
3	8	0	< 1.1
	26		< 1.4
	24		< 1.1
6	20	0	< 1.5
	26		< 1.2
7	24	0	< 1.4
9	12	0	< 1.7
10	10	0	< 1.7
11	18	0	< 1.5
12	16	0	< 1.5
	18		< 1.4
	22		< 0.8
13	14	0	< 1.5
14	12	0	< 1.5
15	4	0	< 1.6
	6		< 2.5
	12		< 1.3
16	2	0	< 1.4
18	2	0	< 0.8
[illegible]	0	1	< 3.8
17			< 2.6
0	10	1	< 1.7
	11		< 1.8

h	k	l	Fo
0	18	1	< 2.1
	23		< 2.3
	25		< 2.1
	28		< 1.5
	29		< 1.1
1	17	1	< 4.0
	20		< 4.2
	21		< 4.2
	23		< 4.1
	25		< 3.7
	26		< 3.4
	27		< 3.0
	28		< 2.6
	29		< 1.9
2	22	1	< 4.2
	23		< 4.1
	24		< 3.9
	25		< 3.7
	26		< 3.3
	27		< 3.0
	28		< 2.5
	29		< 1.8
3	8	1	< 2.7
	13		< 3.5
	14		< 3.7
	16		< 3.9

h	k	l	Fo
3	19	1	< 4.2
	20		< 4.3
	22		< 4.2
	23		< 4.1
	24		< 3.9
	25		< 3.6
	26		< 3.2
	27		< 2.9
	28		< 2.4
	29		< 1.4
4	7	1	< 2.7
	19		< 4.2
	20		< 4.2
	25		< 3.5
	26		< 3.1
	27		< 2.7
	28		< 2.1
5	12	1	< 3.6
	24		< 3.6
	25		< 3.3
	26		< 3.0
	27		< 2.5
	28		< 1.5
6	17	1	< 4.2
	23		< 3.7
	24		< 3.5

h	k	l	Fo
6	25	1	< 3.1
	26		< 2.7
	27		< 2.1
7	5	1	< 3.2
	6		< 3.6
	7		< 3.4
	22		< 3.7
	23		< 3.5
	24		< 3.2
	25		< 2.8
	26		< 2.4
	27		< 1.5
8	4	1	< 3.5
	6		< 3.6
	11		< 4.0
	12		< 4.1
	16		< 4.3
	17		< 4.2
	18		< 4.2
	21		< 3.7
	22		< 3.5
	23		< 3.2
	24		< 2.9
	25		< 2.5
	26		< 1.7
9	2	1	< 3.7

h	k	l	Fo
9	3	1	< 3.7
	4		< 3.8
	7		< 3.9
	8		< 4.0
	10		< 4.1
	13		< 4.2
	14		< 4.3
	15		< 4.2
	16		< 4.2
	17		< 4.3
	18		< 4.1
	19		< 3.9
	20		< 3.7
	22		< 3.2
	23		< 2.9
	24		< 2.5
	25		< 1.8
10	1	1	< 3.9
	4		< 4.0
	5		< 4.0
	7		< 4.1
	9		< 4.2
	10		< 4.2
	11		< 4.3
	12		< 4.3
	13		< 4.3

h	k	l	Fo
10	14	1	< 4.2
	15		< 4.3
	16		< 4.1
	17		< 4.0
	18		< 3.8
	19		< 3.7
	20		< 3.6
	22		< 2.8
	23		< 2.4
	24		< 1.8
11	7	1	< 4.2
	8		< 4.3
	12		< 4.3
	13		< 4.3
	17		< 3.7
	18		< 3.6
	19		< 3.3
	20		< 3.0
	21		< 2.7
	22		< 2.3
	23		< 1.8
12	3	1	< 4.2
	6		< 4.3
	10		< 4.3
	11		< 4.3
	8		< 4.4

h	k	l	Fo	h	k	l	Fo	h	k	l	Fo	h	k	l	Fo	h	k	l	Fo	h	k	l	Fo
12	15	1	< 3.8	16	9	1	< 2.7	3	20	2	< 5.0	8	9	2	< 5.0	11	16	2	< 4.3	16	1	2	< 3.1
	16		< 3.6		10		< 2.5		21		< 4.9		11		< 5.1		17		< 3.9		2		< 3.1
	17		< 3.4		11		< 2.3		22		< 4.6		13		< 5.1		18		< 3.6		3		< 3.0
	18		< 3.2		12		< 2.0		23		< 4.4		14		< 5.1		19		< 3.3		4		< 2.9
	19		< 2.9		13		< 1.5		24		< 4.0		15		< 5.1		20		< 2.6		5		< 2.7
	20		< 2.5	17	1	1	< 2.6		25		< 3.6		16		< 5.0		21		< 2.1		6		< 2.5
	21		< 2.1		2		< 2.6		26		< 3.0		17		< 4.9	12	1	2	< 5.1		7		< 2.3
13	1	1	< 4.2		3		< 2.5		27		< 2.0		18		< 4.7		2		< 5.1		8		< 1.8
	6		< 4.2		4		< 2.5	4	8	2	< 3.9		19		< 4.6		7		< 5.0	0	1	3	< 2.2
	8		< 4.1		5		< 2.4		17		< 5.2		20		< 4.2		9		< 4.8		6		< 2.3
	11		< 3.9		6		< 2.2		18		< 5.2		21		< 3.9		10		< 4.7		17		< 2.2
	12		< 3.8		7		< 2.1		19		< 5.1		22		< 3.4		11		< 4.6		18		< 2.1
	13		< 3.7		8		< 1.8		20		< 4.9		23		< 2.9		12		< 4.5		23		< 1.3
	14		< 3.6		9		< 1.3		21		< 4.8		24		< 2.4		13		< 4.3		24		< 1.0
	15		< 3.4	10	0	2	< 5.8		23		< 4.7	9	1	2	< 4.8		14		< 4.1	1	2	3	< 3.6
	16		< 3.2	12			< 5.8		25		< 3.4		2		< 4.8		15		< 3.9		5		< 3.6
	17		< 2.9	14			< 3.0		26		< 2.7		3		< 4.9		16		< 3.6		13		< 3.8
	18		< 2.6	16			< 3.5	5	6	2	< 3.9		4		< 4.9		17		< 3.2		14		< 3.7
	19		< 2.2	0	8	2	< 1.9		9		< 4.3		6		< 5.0		18		< 2.8		15		< 3.7
	20		< 1.8		10		< 2.1		16		< 5.1		8		< 5.1		19		< 2.0		16		< 3.6
14	1	1	< 4.1		11		< 2.1		17		< 5.2		9		< 5.1	13	1	2	< 4.9		17		< 3.5
	2		< 4.1		13		< 2.2		18		< 5.1		10		< 5.1		2		< 4.9		18		< 3.4
	3		< 4.1		14		< 2.3		19		< 5.0		11		< 5.2		3		< 4.8		19		< 3.2
	4		< 4.1		15		< 2.3		20		< 4.8		12		< 5.2		4		< 4.8		20		< 3.0
	5		< 4.0		16		< 2.4		21		< 4.6		13		< 5.1		5		< 4.8		21		< 2.7
	6		< 4.0		20		< 2.3		22		< 4.4		14		< 5.0		6		< 4.7		22		< 2.4
	7		< 3.9		22		< 2.2		26		< 2.3		15		< 4.9		8		< 4.5		23		< 2.1
	8		< 3.8		23		< 2.1	6	2	2	< 3.7		16		< 4.8		9		< 4.0		24		< 1.7
	9		< 3.8		24		< 1.9		3		< 4.0		17		< 4.6		10		< 4.3	2	1	3	< 3.6
	10		< 3.7		25		< 1.7		4		< 4.1		18		< 4.4		11		< 4.1		6		< 3.7
	11		< 3.6		26		< 1.5		5		< 4.2		19		< 4.1		12		< 4.0		11		< 3.8
	12		< 3.4		27		< 1.2		6		< 4.3		20		< 3.8		13		< 3.7		13		< 3.9
	13		< 3.2	1	12	2	< 4.3		7		< 4.3		21		< 3.4		14		< 3.5		14		< 3.7
	14		< 3.1		19		< 5.1		8		< 4.5		22		< 2.9		15		< 3.2		15		< 3.7
	15		< 2.8		20		< 5.1		9		< 4.5		23		< 2.1		16		< 2.8		16		< 3.6
	16		< 2.4		21		< 5.0		15		< 5.2	10	1	2	< 5.0	14	1	2	< 4.5		17		< 3.5
	17		< 2.1		22		< 4.7		17		< 5.1		7		< 5.1		2		< 4.5		18		< 3.3
	18		< 1.6		23		< 4.6		18		< 5.0		9		< 5.3		3		< 4.4		19		< 3.2
15	1	1	< 3.8		24		< 4.1		19		< 4.9		10		< 5.2		4		< 4.4		20		< 2.9
	2		< 3.8		25		< 3.7		20		< 4.7		11		< 5.1		5		< 4.3		21		< 2.6
	3		< 3.7		26		< 3.2		21		< 4.5		12		< 5.1		6		< 4.2		22		< 2.3
	4		< 3.7		27		< 3.5	7	3	2	< 4.4		13		< 5.0		7		< 4.1		23		< 1.9
	5		< 3.7	2	15	2	< 4.9		4		< 4.3		14		< 5.0		8		< 4.0		24		< 1.0
	6		< 3.6		16		< 5.0		5		< 4.4		15		< 4.9		9		< 3.9	3	3	3	< 5.2
	7		< 3.6		17		< 5.1		6		< 4.5		16		< 4.7		10		< 3.7		5		< 5.3
	8		< 3.3		18		< 5.2		9		< 4.6		17		< 4.3		11		< 3.5		6		< 5.3
	9		< 3.2		20		< 5.1		14		< 5.1		18		< 4.0		12		< 3.3		7		< 5.4
	10		< 3.0		21		< 4.9		15		< 5.2		19		< 3.7		13		< 3.0		8		< 5.4
	11		< 2.9		22		< 4.7		16		< 5.1		20		< 3.3		14		< 2.6		9		< 5.3
	12		< 2.7		23		< 4.5		17		< 5.0		21		< 2.8		15		< 1.8		12		< 5.2
	13		< 2.4		24		< 4.1		18		< 4.9		22		< 1.8	15	1	2	< 3.9		13		< 5.2
	14		< 2.2		25		< 3.7		19		< 4.7	11	1	2	< 5.1		2		< 3.9		14		< 5.1
	15		< 2.1		26		< 3.1		20		< 4.5		2		< 5.1		3		< 3.8		15		< 5.0
	16		< 1.2		27		< 2.8		21		< 4.2		3		< 5.2		4		< 3.8		16		< 4.9
16	1	1	< 3.3	3	10	2	< 4.1		22		< 3.9		6		< 5.1		5		< 3.7		17		< 4.7
	2		< 3.3		13		< 4.6		25		< 0.6		9		< 5.1		6		< 3.6		18		< 4.6
	3		< 3.2		14		< 4.8	8	2	2	< 4.6		10		< 5.0		7		< 3.4		19		< 4.5
	4		< 3.2		15		< 5.0		4		< 4.7		11		< 4.9		8		< 3.3		20		< 4.1
	5		< 3.1		16		< 5.1		5		< 4.7		12		< 4.8		9		< 3.1		21		< 3.7
	6		< 3.0		17		< 5.1		6		< 4.8		13		< 4.7		10		< 2.8		22		< 3.1
	7		< 3.0		18		< 5.2		7		< 4.5		14		< 4.5		11		< 2.5		23		< 2.6
	8		< 2.8		19		< 5.1		8		< 4.9		15		< 4.3		12		< 2.0	4	4	3	< 5.4

h	k	l	F_o
4	5	3	< 5.5
	6		< 5.5
	7		< 5.5
	8		< 5.5
	13		< 5.5
	16		< 5.1
	17		< 4.9
	18		< 4.7
	19		< 4.4
	20		< 4.1
	21		< 3.7
	22		< 3.1
	23		< 2.3
5	5	3	< 4.2
	7		< 4.3
	12		< 4.2
	13		< 4.2
	14		< 4.1
	15		< 4.0
	16		< 3.8
	17		< 3.7
	18		< 3.4
	19		< 3.2
	20		< 2.9
	21		< 2.5
	22		< 2.0
6	4	3	< 4.4
	5		< 4.4
	6		< 4.4
	7		< 4.4
	8		< 4.4
	11		< 4.4
	12		< 4.3
	13		< 4.3
	16		< 3.8
	17		< 3.7
	18		< 3.4
	19		< 3.1
	20		< 2.8
	21		< 2.1
	22		< 1.4
7	1	3	< 4.5
	2		< 4.5
	5		< 4.5
	6		< 4.5
	7		< 4.5
	10		< 4.4
	11		< 4.4
	12		< 4.3
	13		< 4.2
	14		< 4.0
	15		< 3.9
	16		< 3.7
	17		< 3.5
	18		< 3.2
	19		< 2.8
	20		< 2.4
	21		< 1.8
2	2	5	< 2.0
3	2	5	< 2.3

h	k	l	F_o
8	0	3	< 7.0
	1		< 7.0
	2		< 7.0
	3		< 7.0
	4		< 7.0
	5		< 7.0
	6		< 7.0
	7		< 6.9
	8		< 6.8
	9		< 6.8
	10		< 6.6
	11		< 6.5
	12		< 6.4
	13		< 6.1
	14		< 5.8
	15		< 5.5
	16		< 5.2
	17		< 4.9
	18		< 4.4
	19		< 3.7
	20		< 2.7
9	0	3	< 6.9
	1		< 6.9
	2		< 6.9
	3		< 6.9
	4		< 6.8
	5		< 6.8
	6		< 6.8
	7		< 6.7
	8		< 6.6
	9		< 6.4
	10		< 6.3
	11		< 6.1
	12		< 5.9
	13		< 5.7
	14		< 5.4
	15		< 5.1
	16		< 4.6
	17		< 4.2
	18		< 3.5
	19		< 2.5
10	1	3	< 6.6
	2		< 6.6
	3		< 6.6
	4		< 6.6
	5		< 6.5
	6		< 6.4
	7		< 6.3
	8		< 6.2
	9		< 6.0
	10		< 5.8
	11		< 5.6
	12		< 5.4
	13		< 5.1
	14		< 4.8
	15		< 4.4
	16		< 3.8
	17		< 3.0
2	3	5	< 2.6
3	3	5	< 1.9

h	k	l	F_o
11	0	3	< 6.3
	1		< 6.3
	2		< 6.2
	3		< 6.2
	4		< 6.1
	5		< 6.0
	6		< 6.0
	7		< 5.8
	8		< 5.7
	9		< 5.5
	10		< 5.3
	11		< 5.1
	12		< 4.8
	13		< 4.4
	14		< 4.0
	15		< 3.4
	16		< 2.5
12	1	3	< 5.7
	2		< 5.7
	3		< 5.6
	4		< 5.6
	5		< 5.4
	6		< 5.3
	7		< 5.2
	8		< 5.1
	9		< 4.9
	10		< 4.6
	11		< 4.3
	12		< 3.9
	13		< 3.4
	14		< 2.5
13	0	3	< 5.1
	1		< 5.1
	2		< 5.1
	3		< 5.0
	4		< 4.9
	5		< 4.8
	6		< 4.6
	7		< 4.5
	8		< 4.3
	9		< 4.0
	10		< 3.6
	11		< 3.1
	12		< 2.4
14	1	3	< 4.3
	2		< 4.2
	3		< 4.1
	4		< 4.0
	5		< 3.9
	6		< 3.7
	7		< 3.3
	8		< 3.0
	9		< 2.2
0	2	4	< 2.3
	3		< 2.3
	4		< 2.3
	5		< 2.3
	6		< 2.3
2	4	5	< 2.3

h	k	l	F_o
0	7	4	< 2.2
	8		< 2.2
	9		< 2.1
	13		< 1.9
	14		< 1.5
	17		< 1.3
	18		< 1.1
1	2	4	< 3.6
	3		< 3.6
	4		< 3.6
	5		< 3.6
	6		< 3.5
	7		< 3.5
	8		< 3.4
	9		< 3.4
	13		< 2.9
	14		< 2.7
	15		< 2.5
	16		< 2.3
	17		< 2.0
	18		< 1.5
2	0	4	< 3.6
	1		< 3.6
	2		< 3.6
	3		< 3.6
	4		< 3.6
	5		< 3.5
	6		< 3.5
	7		< 3.5
	8		< 3.4
	12		< 3.0
	13		< 2.8
	14		< 2.6
	15		< 2.5
	16		< 2.2
	17		< 1.8
	18		< 1.3
3	1	4	< 4.9
	2		< 4.9
	3		< 4.9
	4		< 4.8
	5		< 4.8
	6		< 4.7
	7		< 4.7
	8		< 4.6
	9		< 4.6
	10		< 4.3
	11		< 4.2
	12		< 4.0
	13		< 3.8
	14		< 3.5
	15		< 3.0
	16		< 2.9
	17		< 2.2
	18		< 1.2
4	0	4	< 5.2
	1		< 5.2
	2		< 5.2
2	5	5	< 1.5

h	k	l	F_o
4	3	4	< 5.1
	4		< 5.1
	5		< 5.1
	6		< 5.0
	7		< 4.9
	8		< 4.8
	9		< 4.7
	10		< 4.5
	11		< 4.3
	12		< 4.1
	13		< 3.9
	14		< 3.6
	15		< 3.4
	16		< 2.7
	17		< 2.1
5	1	4	< 3.9
	2		< 3.9
	3		< 3.8
	4		< 3.8
	5		< 3.7
	6		< 3.7
	7		< 3.6
	8		< 3.6
	9		< 3.4
	10		< 3.3
	11		< 3.2
	12		< 3.0
	13		< 2.8
	14		< 2.5
	15		< 2.2
	16		< 1.7
6	0	4	< 3.9
	1		< 3.9
	2		< 3.8
	3		< 3.8
	4		< 3.7
	5		< 3.7
	6		< 3.6
	7		< 3.5
	8		< 3.4
	9		< 3.2
	10		< 3.1
	11		< 2.9
	12		< 2.6
	13		< 2.3
	14		< 2.0
	15		< 1.0
7	1	4	< 3.7
	2		< 3.7
	3		< 3.7
	4		< 3.6
	5		< 3.6
	6		< 3.5
	7		< 3.4
	8		< 3.3
	9		< 3.2
	10		< 3.0
	11		< 2.8
3	0	5	< 2.5

h	k	l	F_o
7	12	4	< 4.4
	13		< 4.4
	14		< 4.4
8	0	4	< 5.4
	1		< 5.4
	2		< 5.4
	3		< 5.3
	4		< 5.3
	5		< 5.1
	6		< 5.0
	7		< 4.8
	8		< 4.4
	9		< 4.4
	10		< 4.1
	11		< 3.7
	12		< 3.3
	13		< 2.4
9	1	4	< 4.8
	2		< 4.8
	3		< 4.8
	4		< 4.7
	5		< 4.5
	6		< 4.4
	7		< 4.3
	8		< 3.9
	9		< 3.6
	10		< 3.2
	11		< 2.5
10	0	4	< 4.1
	1		< 4.1
	2		< 4.1
	3		< 4.0
	4		< 3.9
	5		< 3.7
	6		< 3.5
	7		< 3.2
	8		< 2.7
	9		< 1.5
11	1	4	< 2.9
	2		< 2.8
	3		< 2.6
	4		< 2.3
	5		< 1.5
0	1	5	< 1.8
	2		< 1.2
	3		< 1.1
	4		< 1.0
	5		< 2.0
	6		< 2.4
	7		< 1.7
1	0	5	< 1.2
	1		< 1.2
	2		< 1.1
	3		< 2.4
	4		< 2.8
	5		< 2.3
	6		< 1.5
2	1	5	< 1.0
3	1	5	< 2.5

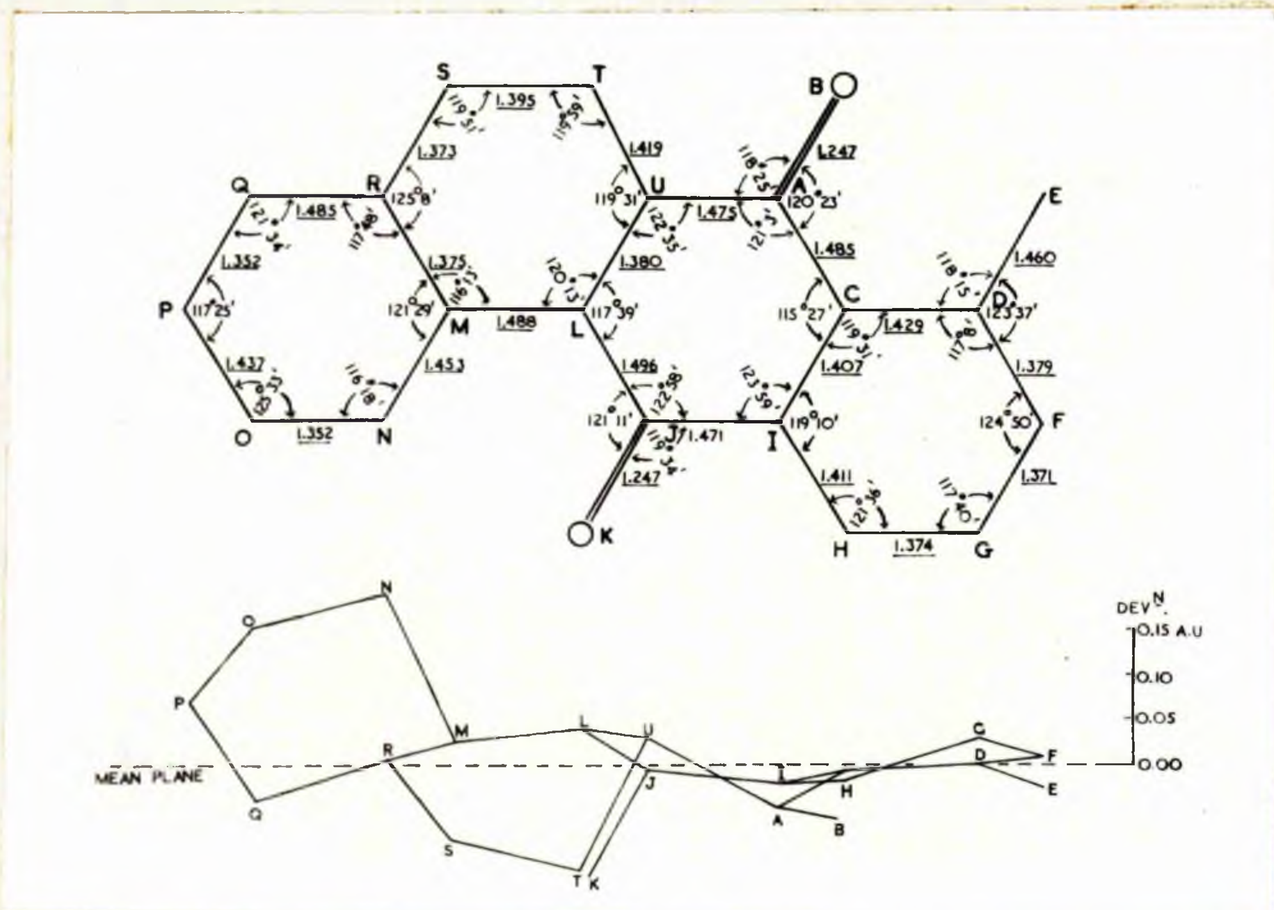


Fig. 3.13. The bond lengths and bond angles of 5-methyl 1:2-benzanthraquinone. The deviations of the atoms from the mean molecular plane are also shown.

(e) <u>Discussion of the Structure.</u>

The final set of co-ordinates given in Table 3,13 was used to calculate the bond lengths and bond angles of 5-methyl 1:2-benzanthraquinone and these are shown in Table 3,17(a) and (b) and illustrated in Fig. 3,13. For comparison, the bond lengths calculated from the co-ordinates used in the initial stage of three-dimensional refinement are also given in Table 3,13(a). The mean bond lengths and bond angles of the aromatic rings are shown below.

AROMATIC RING	MEAN BOND LENGTH	MEAN BOND ANGLE
CDFGHI	1.395 A.U.	119°52'
STULMR	1.405 A.U.	120°7'
KMNOPQ	1.409 A.U.	120°2'

The overall mean aromatic bond length is 1.405 A.U. and the mean aromatic bond angle is 120°0'.

The principle of least squares was used to calculate the mean molecular plane, which was found to be

$$0.0314x - 0.4398y + 0.8975z + 0.9311 = 0$$

TABLE 3.17.

(a) The calculated bond lengths of 5-methyl 1:2-benzanthraquinone and their standard deviations (σ). The bond length values quoted in brackets were those calculated from the co-ordinates used in the initial cycle of three-dimensional least squares refinement.

(Values in A.U.)

BOND	BOND LENGTH		σ	BOND	BOND LENGTH		σ
AB	1.247	(1.146)	0.019	JL	1.496	(1.591)	0.026
AC	1.485	(1.563)	0.022	LU	1.380	(1.422)	0.024
AU	1.475	(1.488)	0.021	ML	1.488	(1.448)	0.024
DE	1.460	(1.402)	0.028	MR	1.375	(1.328)	0.024
DC	1.429	(1.398)	0.021	MN	1.453	(1.496)	0.027
DF	1.379	(1.422)	0.026	ON	1.352	(1.388)	0.028
GF	1.371	(1.293)	0.028	OP	1.437	(1.433)	0.030
GH	1.374	(1.342)	0.024	QP	1.352	(1.327)	0.030
IH	1.411	(1.504)	0.025	QR	1.485	(1.507)	0.024
IC	1.407	(1.435)	0.023	SR	1.373	(1.444)	0.023
IJ	1.471	(1.371)	0.023	ST	1.395	(1.380)	0.022
JK	1.247	(1.276)	0.024	TU	1.419	(1.431)	0.024

Mean aromatic bond length = 1.405 A.U.

TABLE 3.17.

(b) The calculated bond angles of 5-methyl 1:2-benzanthraquinone and the deviations of the atoms from the mean molecular plane.

BOND ANGLE	ANGLE	BOND ANGLE	ANGLE	ATOM	DEVIATION (A.U.)
UAB	118°25'	KJL	121°11'	B	-0.059
BAC	120°23'	JLM	117°39'	K	-0.120
UAC	121°3'	ULM	120°13'	A	-0.048
ACI	115°27'	LMR	116°13'	C	-0.007
ICD	119°31'	RMN	121°29'	D	0.000
CDE	118°15'	MNO	116°18'	E	-0.025
EDF	123°37'	NOP	125°33'	F	0.010
CDF	117°8'	OPQ	117°25'	G	0.030
DFG	124°50'	PQR	121°34'	H	-0.017
FGH	117°40'	QRM	117°48'	I	-0.022
GHI	121°36'	MRS	125°8'	J	-0.005
HIC	119°10'	RST	119°51'	L	0.039
CIJ	123°59'	STU	119°59'	M	0.024
IJL	122°58'	TUL	119°31'	N	0.187
IJK	119°34'	ULA	122°35'	O	0.150
				P	0.068
				Q	-0.040
				R	0.003
				S	-0.083
				T	-0.117
				U	0.030

The deviations of the atoms from the mean molecular plane are given along with the calculated bond angles in Table 3,17(b) and illustrated in Fig. 3,13. The maximum deviations from the above plane are in the atoms K,N,O,S and T in which the deviations are -0.120, 0.187, 0.150, -0.083 and -0.117 respectively.

There is no direct estimation of the accuracy of the final set of atomic co-ordinates, but the estimated standard deviations (calculated using the standard formula given in the International Tables for X-ray Crystallography, Vol. II) of the previous set of atomic co-ordinates in the three-dimensional refinement are shown in Table 3,18 and these will be used to define the upper limit of the standard deviations of the final atomic co-ordinates.

Since the standard deviations of the co-ordinates vary slightly, the standard deviation of the bond length (σ_L) between two symmetrically independent atoms with co-ordinates (x_1, y_1, z_1), (x_2, y_2, z_2) and standard deviations (σ_{x_1}, σ_{y_1}, σ_{z_1}), (σ_{x_2}, σ_{y_2}, σ_{z_2}) was calculated from the equation (Ahmed and Cruickshank, 1953)

$$\sigma_L^2 = (\sigma_{x_1}^2 + \sigma_{x_2}^2)\cos.^2\alpha + (\sigma_{y_1}^2 + \sigma_{y_2})^2\cos.^2\beta + (\sigma_{z_1}^2 + \sigma_{z_2})^2\cos.^2\gamma$$

where cos.α, cos.β and cos.γ are the direction cosines which the bond makes with crystal axes. The standard deviations of the bond lengths are quoted in Table 3,17(a).

In discussing the structure of 5-methyl 1:2-benzanthraquinone, the

TABLE 3.18.

The estimated standard deviations (σ) of the carbon and oxygen atomic co-ordinates used to calculate the structure factors of the final cycle of the three-dimensional least squares refinement.

ATOM	σ_x (A.U.)	σ_y (A.U.)	σ_z (A.U.)
B	0.0123	0.0108	0.0155
K	0.0127	0.0106	0.0197
A	0.0145	0.0152	0.0176
C	0.0168	0.0124	0.0176
D	0.0177	0.0151	0.0174
E	0.0224	0.0188	0.0210
F	0.0208	0.0162	0.0152
G	0.0204	0.0171	0.0154
H	0.0180	0.0171	0.0201
I	0.0172	0.0155	0.0173
J	0.0209	0.0156	0.0205
L	0.0182	0.0141	0.0184
M	0.0187	0.0139	0.0165
N	0.0205	0.0183	0.0222
O	0.0206	0.0160	0.0295
P	0.0233	0.0169	0.0185
Q	0.0210	0.0165	0.0224
R	0.0164	0.0146	0.0181
S	0.0168	0.0156	0.0165
T	0.0174	0.0147	0.0197
U	0.0167	0.0142	0.0171
MEAN	0.0183	0.0152	0.0189

specified levels of significance recommended by Cruickshank (Cruickshank, 1949) will be used. If a bond A, standard deviation σ_A, is determined as longer than a bond B, standard deviation σ_B, by an amount δl, then the criterion which Cruickshank recommends should be adopted is as follows. Let P be the probability that A could be observed greater than B by chance, although it is really equal to B, then if

$P > 5\%$ δl is not significant

$5\% > P > 1\%$ δl is possibly significant

$P \leqslant 1\%$ δl is significant.

It can be shown that if

$$\delta l/(\sigma_A^2 + \sigma_B^2)^{\frac{1}{2}} = \sqrt{2}.x$$

then $$P = \tfrac{1}{2}(1 - \text{erf}.x)$$

The values of the bond lengths AC,AU,JI,JL are in good agreement with the single C – C bond length of about 1.51 A.U. quoted for this type of structure. The value of the bond lengths AB and JK (1.247 A.U.) are significantly longer than the value of the C = O bond length given in the Table of Interatomic Distances (T.I.C., 1958) in which the value of 1.15 ± 0.02 A.U. is quoted as a mean for the paraquinone structures $C_6Br_4O_2$, $C_6Cl_4O_2$, $C_6H_4O_2$ and $C_6I_4O_2$. The value of 1.15 A.U. is also quoted for the C = O bond length in the structure of anthraquinone (Sen, 1948). The value of 1.247 A.U. for the bond lengths agrees much more closely with the values of, 1.25 A.U. quoted

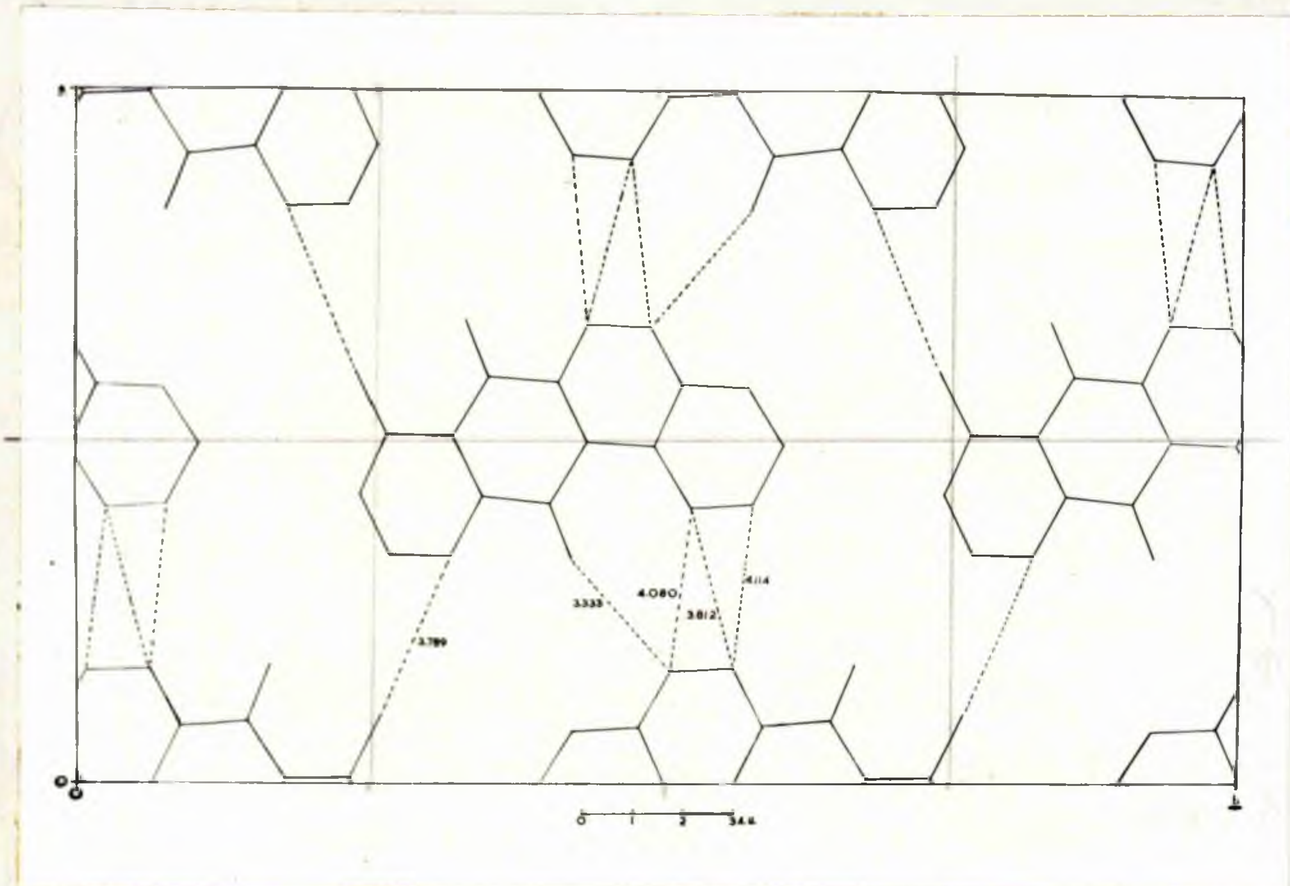


Fig. 3.14. The projection of the contents of the unit cell down the $\underline{c}$ - axis showing the intermolecular contact of < 4.20 A.U.

in structure of dichloroanthraquinone (Bailey, 1958), 1.22 A.U. quoted in the structure of Indanthrone (Bailey, 1955), and 1.21 A.U. quoted in the structure of Flavanthrone (Stadler, 1953). The mean C – C aromatic bond length in the structure is 1.405 A.U. and using this value, the bond length LM is such that $\delta 1 = 0.083$ A.U. and P = 0.004%, which implies that the bond length LM is significantly longer than the mean bond length. In the same way it can be shown that the bond length QR is also significantly longer than the mean. The bond lengths QP and NO are possibly significantly shorter and the bond length MN is possibly significantly longer than the mean.

In comparing the bond lengths calculated at the end of the two-dimensional least squares refinement with the final values (Table 3,17(a)), it can be seen that the bond lengths AB, AC, FG, IH, KJ, and JL have changed by a surprisingly large amount considering that the mean standard deviation of the former set was of the order of 0.036 A.U.

An investigation of the significance of the deviations of the atoms from the mean molecular plane showed that the deviations of the atoms B,K,A,N,O,P,S, and T are all significant.

The packing arrangement of the molecules in the unit cell is illustrated in Fig. 3,14 and the intermolecular contacts of < 4.20 A.U. are drawn. The values of the C – C intermolecular contacts are typical of compounds of this type and the value of 3.33 A.U. for the C – O intermolecular contact is very similar to the values of C – O intermolecular contacts reported in structures of dichloroanthraquinone, flavanthrone and indanthrone.

The final set of values U_{ij} show that definite anisotropy exists in the thermal motions of the atoms, but a full discussion of the temperature effect is not possible at this stage of the refinement, because the standard deviations of the terms U_{12}, U_{13}, U_{23} are still very large. The mean standard deviations of the U_{ij}'s used in the last cycle of refinement are shown below.

$\sigma_{U_{11}} = 0.0099$ A.U.^{2} $\sigma_{U_{22}} = 0.0078$ A.U.^{2} $\sigma_{U_{33}} = 0.0115$ A.U.^{2}

$\sigma_{U_{12}} = 0.0154$ A.U.^{2} $\sigma_{U_{23}} = 0.0180$ A.U.^{2} $\sigma_{U_{13}} = 0.0278$ A.U.^{2}

In a recent paper Murty (Murty, 1957) has stated that the carbon and oxygen atoms of the C = O group in anthraquinone have different scattering factor curves from the normal carbon and oxygen atoms and he has prepared scattering curves for these atoms derived by an empirical method from the contours of the electron density map of the well resolved (h01) projection of that compound. He found that the oxygen atom was in a partially ionised state having nine electrons, whereas the carbon atom bonded to the oxygen had only 5 electrons. It was decided to investigate 5-methyl 1:2-benzanthraquinone to see if a similar effect occurred. The method used was to calculate the atomic profiles of the Murty carbon and oxygen atoms from the equation for the electron density at a distance r from the centre of an atom,

$$(r) = \int_0^{s_0} 2\pi s.\ f(s).\ J_0\ (2\pi rs.)ds.$$

where f(s) is the value of the atomic scattering factor.

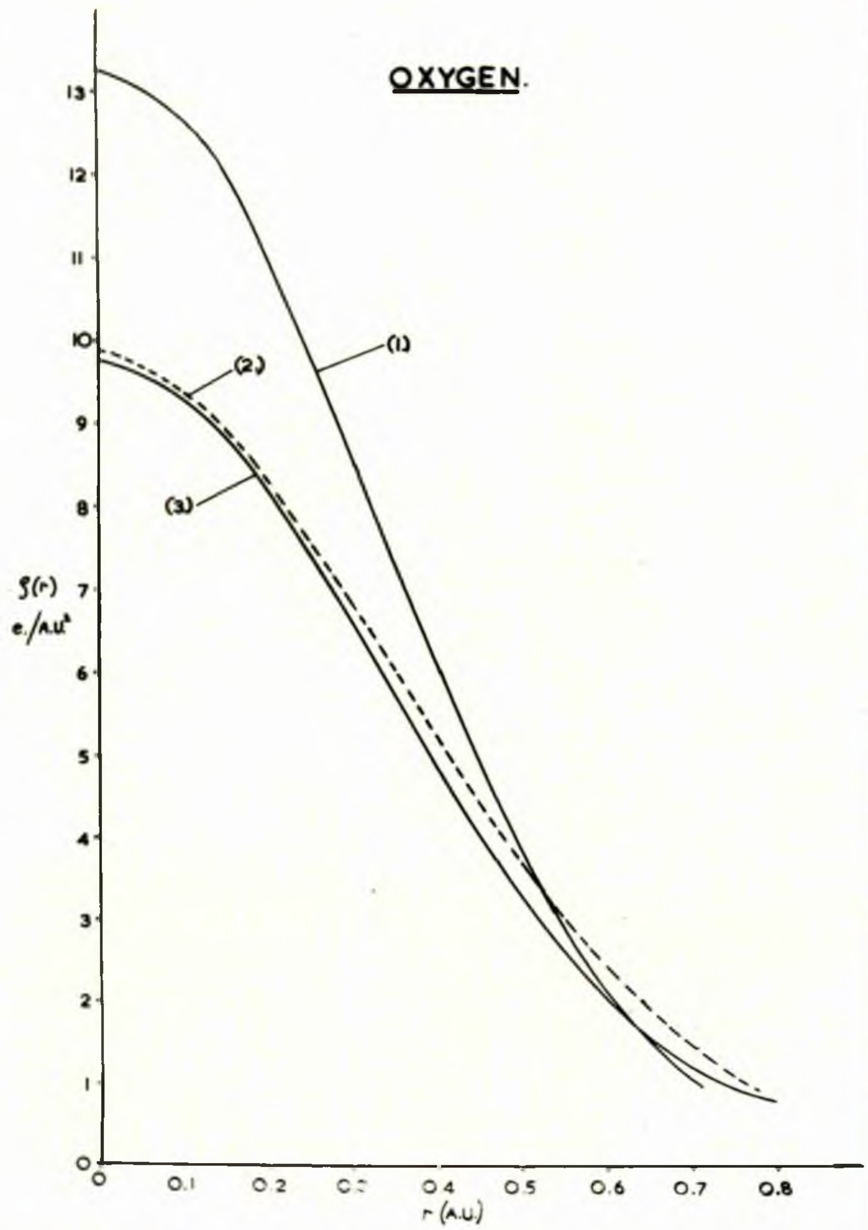


Fig. 3.15. Comparison of the oxygen atomic profiles.

(1) The atomic profile calculated from the Murty scattering curve.

(2) The atomic profile of the atom B obtained from the final electron density map of the (hk0) projection.

(3) The atomic profile calculated from the Berghuis scattering curve with a temperature correction of exp.−(B sin$^2\theta/\lambda^2$), where B = 5.0 A.U.^{2}.

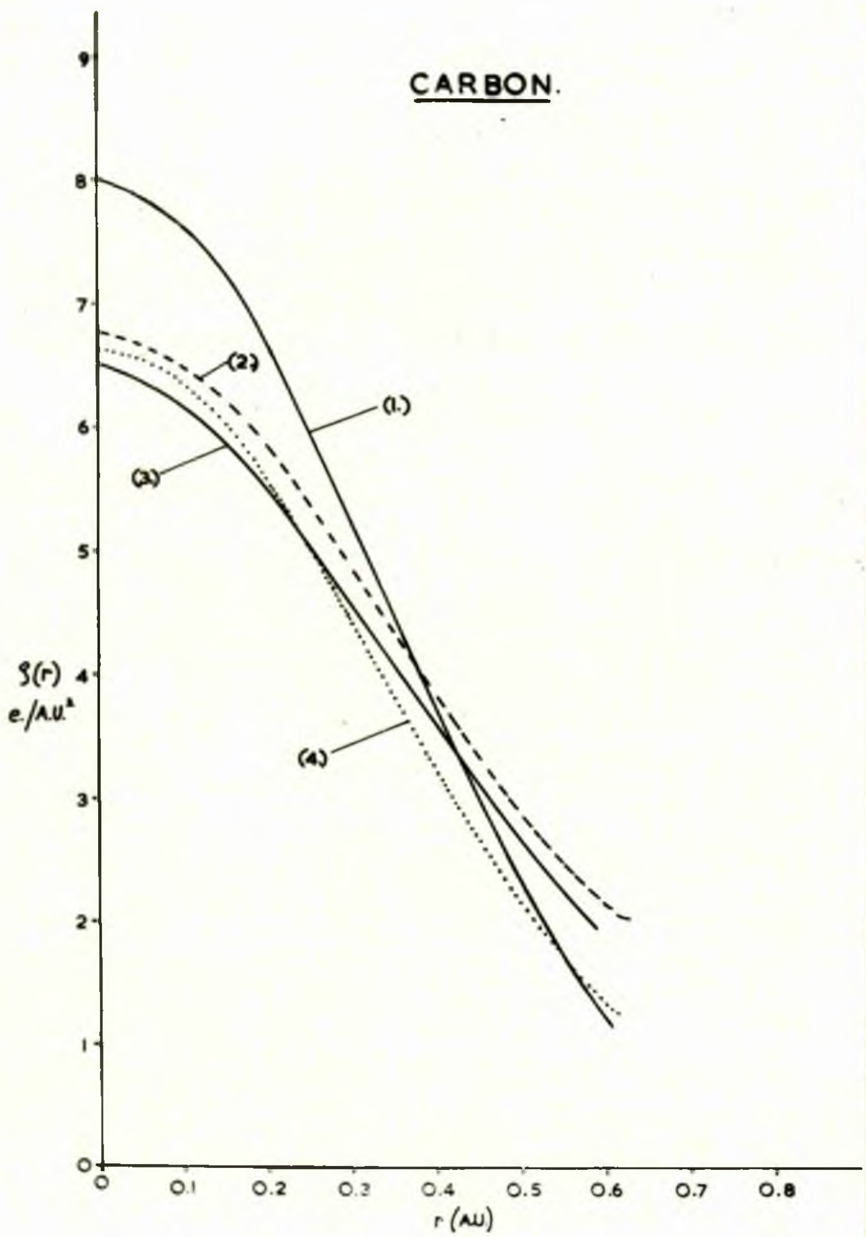


Fig. 3.16. Comparison of the carbon atomic profiles.

(1) The atomic profile calculated from the Murty scattering curve.

(2) The atomic profile of the atom A }
(3) The atomic profile of the atom J } obtained from the final electron density map of the (hk0) projection.

(4) The atomic profile calculated from the Berghuis scattering curve ($B = 4.0$ A.U.^{2}).

This definite integral was solved by numerical integration and the values of $\rho(r)$ for $r = 0, 0.1, \ldots\ldots\ldots, 0.8$ A.U. were obtained. In addition the atomic profile of a carbon and an oxygen atom were calculated using the appropriate Berghuis scattering curves with a temperature correction of exp.$-(B\sin^2\theta/\lambda^2)$, where B = 5.0 A.U.^{2} for the oxygen atom and B = 4.0 A.U.^{2} for the carbon atom. These two theoretical atomic profiles for each atom are compared in Figs. 3,15, 3,16 with the actual atomic profiles obtained from the contours of the final electron density map in Fig. 3,10. In each case the experimental curve agrees much better with the theoretical profile calculated using the Berghuis scattering curve. There is therefore no evidence in the case of 5-methyl 1:2-benzanthraquinone for the effect reported by Murty.

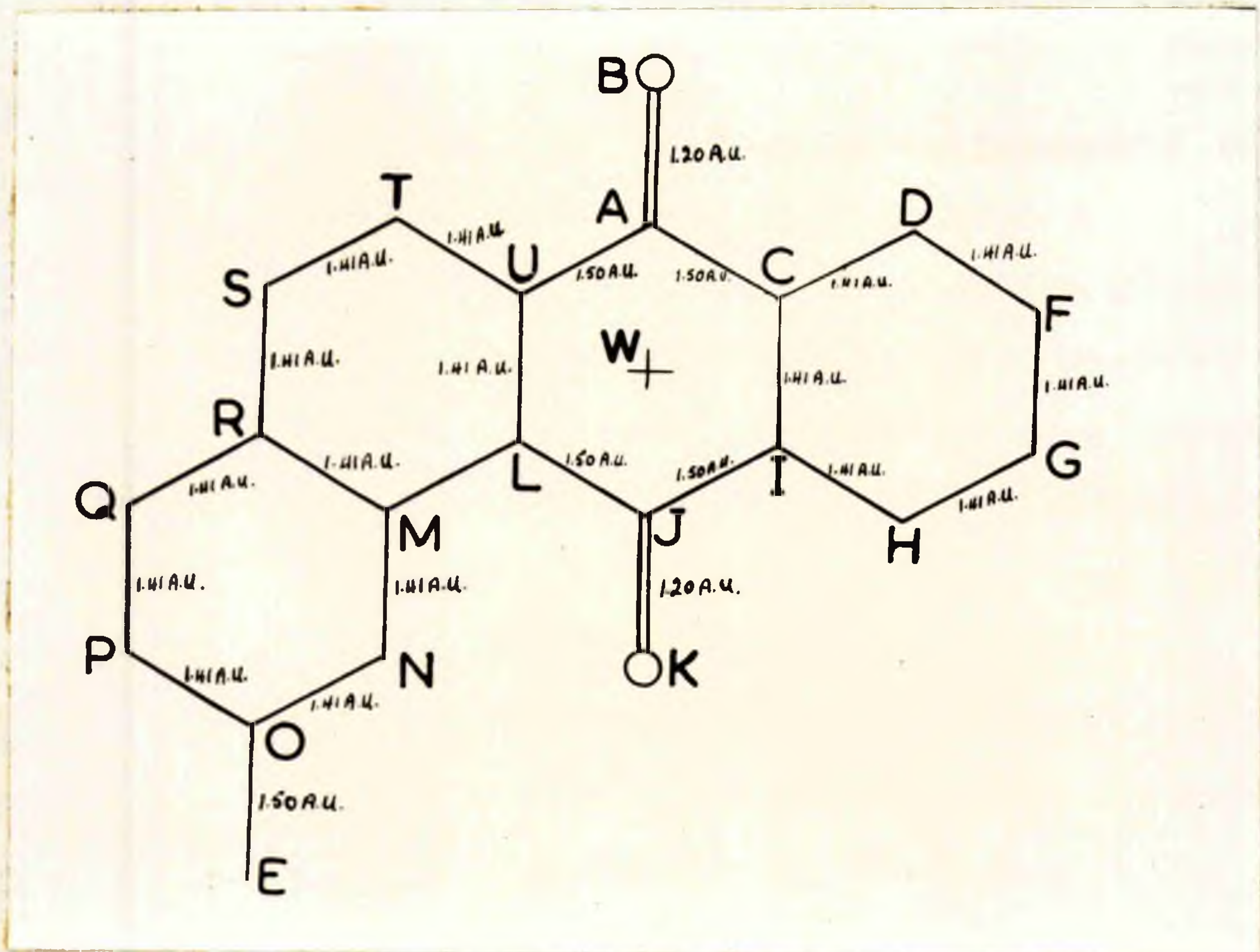


Fig. 4.1. The molecule of 2'-methyl 1:2-benzanthraquinone showing the lettering of the atoms adopted in this investigation. The bond lengths shown were those used in the initial stages of the structure determination.

CHAPTER IV.

THE STRUCTURE OF

2'-METHYL 1:2-BENZANTHRAQUINONE ($C_{19}O_2H_{12}$).

(a) Preliminary Discussion.

A sketch of the molecule is shown in Fig. 4,1. The lettering as indicated in the diagram will be followed throughout this chapter. The position in the molecule indicated by W will be referred to as the molecular centre. The expected bond lengths which were used in the initial stages of the investigation are also shown in the diagram.

The details of the space-group and unit cell dimensions of the yellow needle-shaped crystals are given in Chapter II section j (form I). The space-group is $P2_1$ and the cell dimensions are:

$\underline{a}$ = 20.674 ± 0.020 A.U.

$\underline{b}$ = 4.06 ± 0.02 A.U. β = 90.80 ± 0.05°

$\underline{c}$ = 7.768 ± 0.008 A.U.

There are two molecules in the unit cell, the molecular weight is 272.26 and F(000) = 284.

As in the case of 5-methyl 1:2-benzanthraquinone the molecule possesses no centre of symmetry and hence the asymmetric unit is one molecule, consisting of 19 carbon atoms, 2 oxygen atoms and 12 hydrogen atoms.

Equi-inclination photographs were taken about the b and c - axes of rotation and the first three upper layer lines of the b - axis were also photographed. No photographs were taken about the a - axis of rotation because a suitable crystal could not be found. All reflection intensities were measured visually and in addition the (h0l) reflections were measured on the Geiger counter spectrometer and the upper layer line intensities of the b - axis were measured on the microdensitometer. The intensities were corrected and put on the same scale using the technique described in Chapter III section (a). Wilson's method to determine the absolute scale factor was applied to the intensities of the (h0l) zone and the resulting graph indicated a temperature factor (B) of approximately 4.5 A.U.^{2} and a scale factor of 0.86 to put the observed structure factors on the absolute scale. This scale factor was later found to be within 15% of the correct scale factor.

(b) The Determination of the Approximate Structure.

(i) Direct Method.

Before starting on the long process of trial and error methods of finding an approximate structure, it was decided to apply the direct method of Harker-Kasper Inequalities (Harker and Kasper, 1948) to the structure factors of the (h0l) zone, in which the atoms should be well resolved (b = 4.06 A.U.).

Schwartz's inequality is

$$\left|\int f.g.dv\right|^2 \leq \left(\int |f|^2 dv\right)\left(\int |g|^2 dv\right)$$

where f and g are functions in a space in which dv is a volume element. When this inequality is applied to the equation defining the structure factor, further inequalities are obtained (Gillis, 1948). The most useful of these inequalities was found to be,

$$(U_H \pm U_{H'})^2 \leq (1 \pm U_{H+H'})(1 \pm U_{H-H'})$$

where $U_H = U(h,0,l)$ $\qquad U_{H+H'} = U(h+h',0,l+l')$

$U_{H'} = U(h',0,l')$ $\qquad U_{H-H'} = U(h-h',0,l-l')$

and U(h,0,l) is the unitary structure factor of reflection h0l . The application of the above relationship leads to results of the type,

$$S(h+h',0,l+l') = S(h,0,l)\ S(h',0,l')$$

where S means "the sign of".

When the above inequalities were applied in a systematic manner to the unitary structure factors of the (h0l) zone, a set of five equations was obtained involving the signs of only eleven structure factors. These equations are given in Table 4,1 and the relationships which were later found to be incorrect are marked with a cross. No phases were determined uniquely and the method failed to give enough information to solve the structure. This was not surprising, since there are relatively few structure factors with large unitary values. It has been shown (Lipson and Cochran, 1953) that, if p is the number of equivalent positions and m is the number of atoms in the asymmetric unit, then when N denotes the number of indentical atoms in

TABLE 4.1.

Harker-Kasper sign relationships for 2'-methyl 1:2-benzanthraquinone.

$S(9 0 7)$	=	$S(11\ 0\ 1)\ S(\bar{2}\ 0\ 6)$
$S(\overline{14}\ 0\ 5)$	=	$-S(22\ 0\ 1)^{+}$
$S(23\ 0\ 1)$	=	$-S(13\ 0\ 5)^{+}$
$S(\overline{13}\ 0\ 6)$	=	$S(5\ 0\ 4)\ S(\overline{18}\ 0\ 2)$
	=	$-S(9\ 0\ 8)$

where S means 'the sign of'.

Fig. 4.2. The weighted reciprocal lattice of the (h0l) projection.

the unit cell we have,

$$N = pm \quad \text{and} \quad \overline{U}^2 = \frac{1}{N}$$

Hence if N is large, the value of $\overline{U}$ - the average unitary structure factor - will be small and there will be little likelihood of solving the phase problem by the use of Harker-Kasper inequalities.

(ii) Trial and Error Method.

The weighted reciprocal lattice of the (h0l) zone is shown in Fig. 4,2. The mean benzene ring was reconstructed and this indicated that in this projection, the molecule was tilted through an angle of approximately 30° about a line joining the carbon atoms A and J. There are five possible ways in which the molecule of 2'-methyl 1:2-benzanthraquinone can be built up from the basic benzene unit and once the correct orientation has been determined, the position in the unit cell of the molecular centre must also be found.

It was thought that the best way to obtain this information would be to compute the Patterson function

$$P(u,v,w) = \frac{1}{V} \sum_{-\infty}^{\infty}{}_h \sum_{-\infty}^{\infty}{}_k \sum_{-\infty}^{\infty}{}_l \left| F_o(hkl) \right|^2 \cos 2\pi(hu + kv + lw)$$

which determines the vector relationships between the scattering centres i.e. the atoms (Patterson, 1934). In this case, the two-dimensional (h0l) projection of the Patterson function was derived and the contour map obtained is shown in Fig. 4,3(a). If the

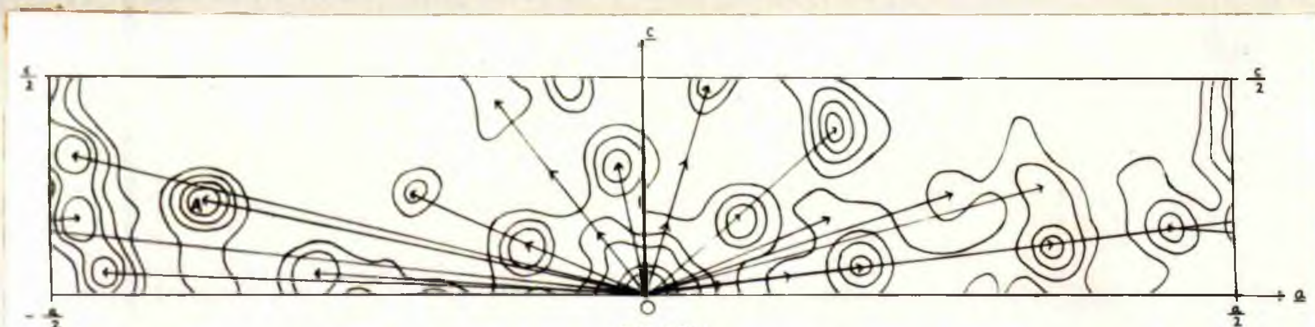


FIG. 4,3(a).

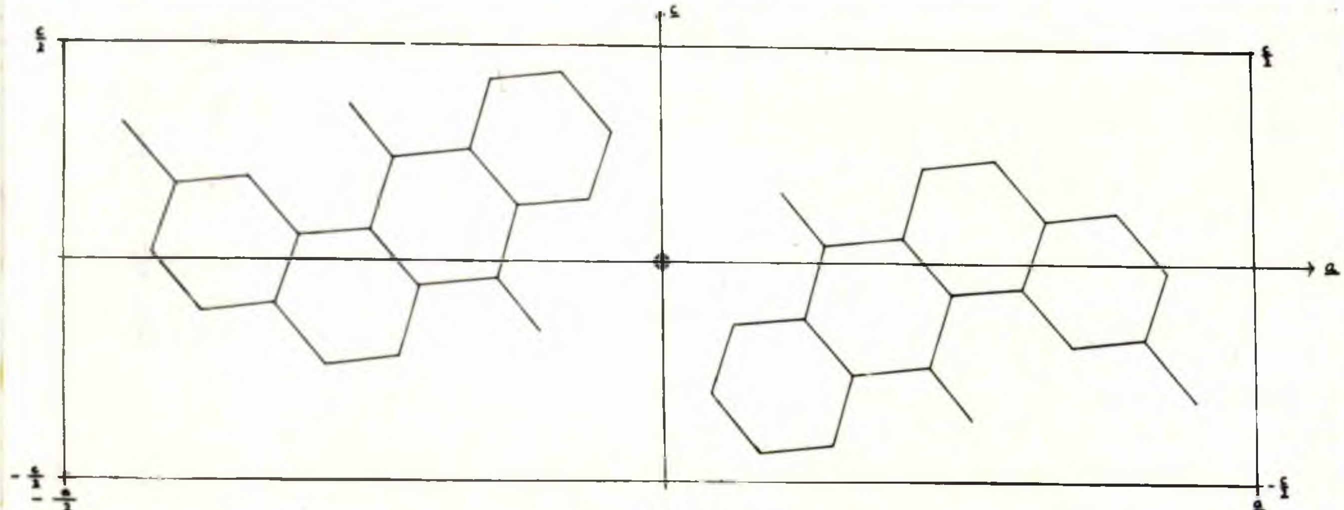


FIG. 4,3(b).

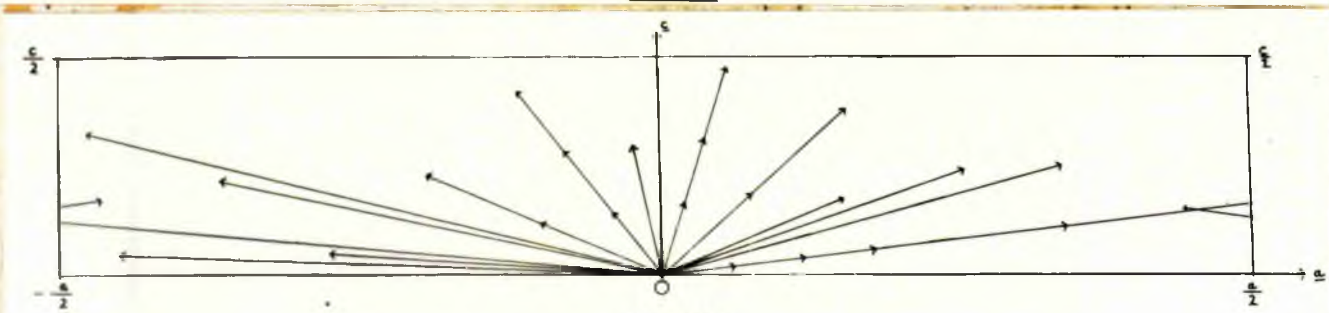


FIG. 4,3(c).

Fig. 4.3. (a) The Patterson map of the b - axis projection. The $|F(000)|^2$ term has been omitted and the contours are drawn at arbitrary intervals. Superimposed on the map is the calculated distribution of peaks from the proposed structure.

(b) The proposed arrangement of the molecules in the (h0l) projection.

(c) The distribution of peaks in the Patterson function obtained from the proposed structure.

molecule of 2'-methyl 1:2-benzanthraquinone is planar, then many of the interatomic vectors may overlap and the actual interpretation of the Patterson map may be relatively easy. By comparing the theoretical vector distribution of each of the five possible orientations with the Patterson map, it appeared that one of the possible orientations was more likely than the others. One high peak (A in Fig. 4,3(a)) had still to be explained. The position and height of the peak were such that it probably represented the set of vectors between corresponding atoms in the anthraquinone parts of the two molecules related by the centre of symmetry at the origin of the projection. This gave the vector distance between the molecular centres of the two molecules in the unit cell. The proposed orientation and arrangement of the molecules in the (h0l) projection are shown in Fig. 4,3(b) and the vector distribution which this proposed structure would give is shown in Fig. 4,3(c). This calculated vector distribution is also shown superimposed on the Patterson map in Fig. 4,3(a) and the fit is remarkably good.

The tilt indicated by the weighted reciprocal lattice was applied to the basic molecule and the co-ordinates of atoms were calculated with the molecular centre at (0.317$\underline{a}$, 0.105$\underline{c}$), as indicated by the Patterson synthesis. These x and z co-ordinates are given in Table 4,2. In the initial stages of the structure determination the hydrogen contribution to the scattering was neglected and an oxygen atom was assumed to have a scattering power $^4/_3$ that of a carbon atom.

TABLE 4.2.

Fractional x and z co-ordinates.

ATOM.	x/a.	z/c.
B	0.402	-0.161
K	0.238	0.361
A	0.364	-0.040
C	0.382	0.127
D	0.443	0.144
E	0.049	0.316
F	0.461	0.299
G	0.418	0.435
H	0.357	0.416
I	0.340	0.258
J	0.276	0.240
L	0.258	0.073
M	0.197	0.056
N	0.154	0.192
O	0.094	0.173
P	0.076	0.018
Q	0.119	-0.119
R	0.179	-0.099
S	0.232	-0.235
T	0.283	-0.216
U	0.300	-0.058

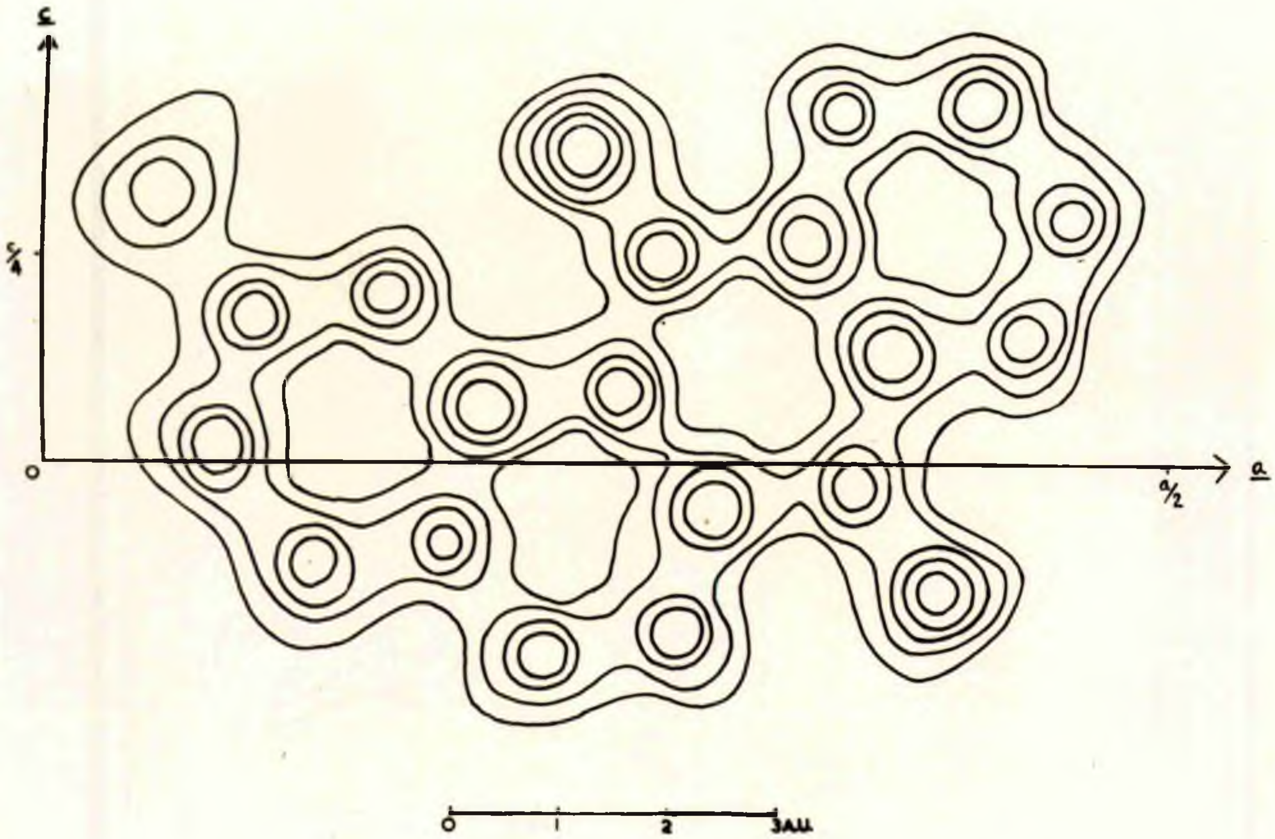


Fig. 4.4. The initial Fourier map of the (h0l) projection. The contours are drawn at arbitrary intervals.

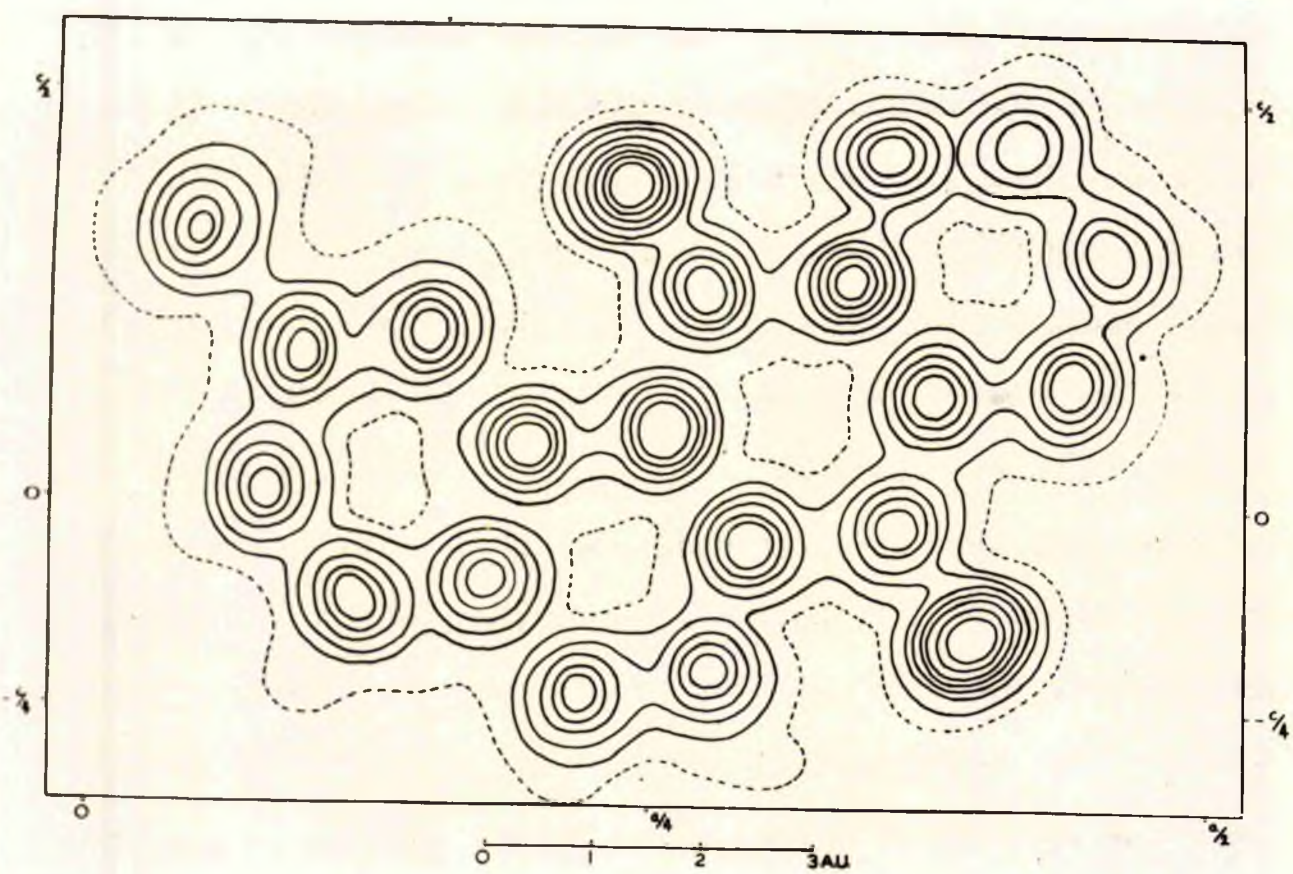


Fig. 4.3. The second Fourier map of the (h0l) projection. The contours are drawn at intervals of 1 e./A.U.^{2}, the 1 e./A.U.^{2} being dotted.

The carbon scattering curve used was that of Berghuis et. al. suitably corrected for the temperature effect. The temperature factor used was B = 4.5 A.U.^{2}.

The structure factors of the (h0l) zone were computed for all reflections with sinθ < 0.65. The observed structure factors were scaled to the calculated values by applying a scale factor of 1.16. The reliability index for the 224 planes which were calculated was 0.30, which seemed most encouraging. The phases of 130 of the largest structure factors were used to compute a Fourier synthesis and the resulting electron density map is shown in Fig. 4,4. All the atoms were well resolved and the co-ordinates of the peaks were extracted using the method of Burns and Iball. The new co-ordinates were used to recalculate the structure factors of all the possible reflections in the (h0l) zone and the reliability index was found to be 0.23. An examination of the phases derived from calculation showed that only one of the structure factors included in the first Fourier synthesis had changed sign. A second Fourier synthesis was now computed including the phases of an additional 92 structure factors. The new co-ordinates were extracted from the electron density map (Fig. 4,5) by the technique already described. The structure factors of the (h0l) zone were recalculated and the reliability index was found to be 0.18.

An attempt was now made to derive the atomic y co-ordinates by examining the structure in the (hk0) projection. Since the **b** - axis is a screw axis, the molecular centre can be placed anywhere along the b - axis. The best agreement between the observed and calculated structure factors was obtained when the y co-ordinates were calculated on the assumption that in the (h01) projection the molecule is planar with tilts of approximately 30° about a line joining the atoms A and J and of 7° about the perpendicular to the line AJ. The y co-ordinates derived in this manner are shown in Table 4,3. The values of the structure factors of the observed (hk0) reflections were calculated and the reliability factor was found to be 0.15.

(c) Refinement of the Structure of 2'-Methyl 1:2-Benzanthraquinone.

Before carrying out a full three-dimensional least squares refinement, one cycle of least squares was computed on the structure factors of the (h01) zone. This was done on the Pegasus computer at Northampton Polytechnic. The x and z co-ordinates used were those derived from the second Fourier map, together with the assumed hydrogen co-ordinates, calculated on the basis of a carbon-hydrogen bond length of 1.05 A.U. On the assumption that the carbon atoms at the centre of the molecule will vibrate less than those on the outer edge, individual isotropic temperature factors were assigned to the atoms as shown in Table 4,4.

TABLE 4.3.

Atomic y co-ordinates used in the first cycle of 3-dimensional least squares refinement.

ATOM.	y/b.	y(A.U.).
B	-0.084	-0.34
K	0.084	0.34
A	-0.042	-0.17
C	-0.179	-0.73
D	-0.348	-1.41
E	0.604	2.45
F	-0.475	-1.93
G	-0.433	-1.76
H	-0.264	-1.07
I	-0.137	-0.56
J	0.042	0.17
L	0.179	0.73
M	0.348	1.41
N	0.390	1.58
O	0.559	2.27
P	0.686	2.79
Q	0.644	2.61
R	0.475	1.93
S	0.433	1.76
T	0.264	1.07
U	0.137	0.56

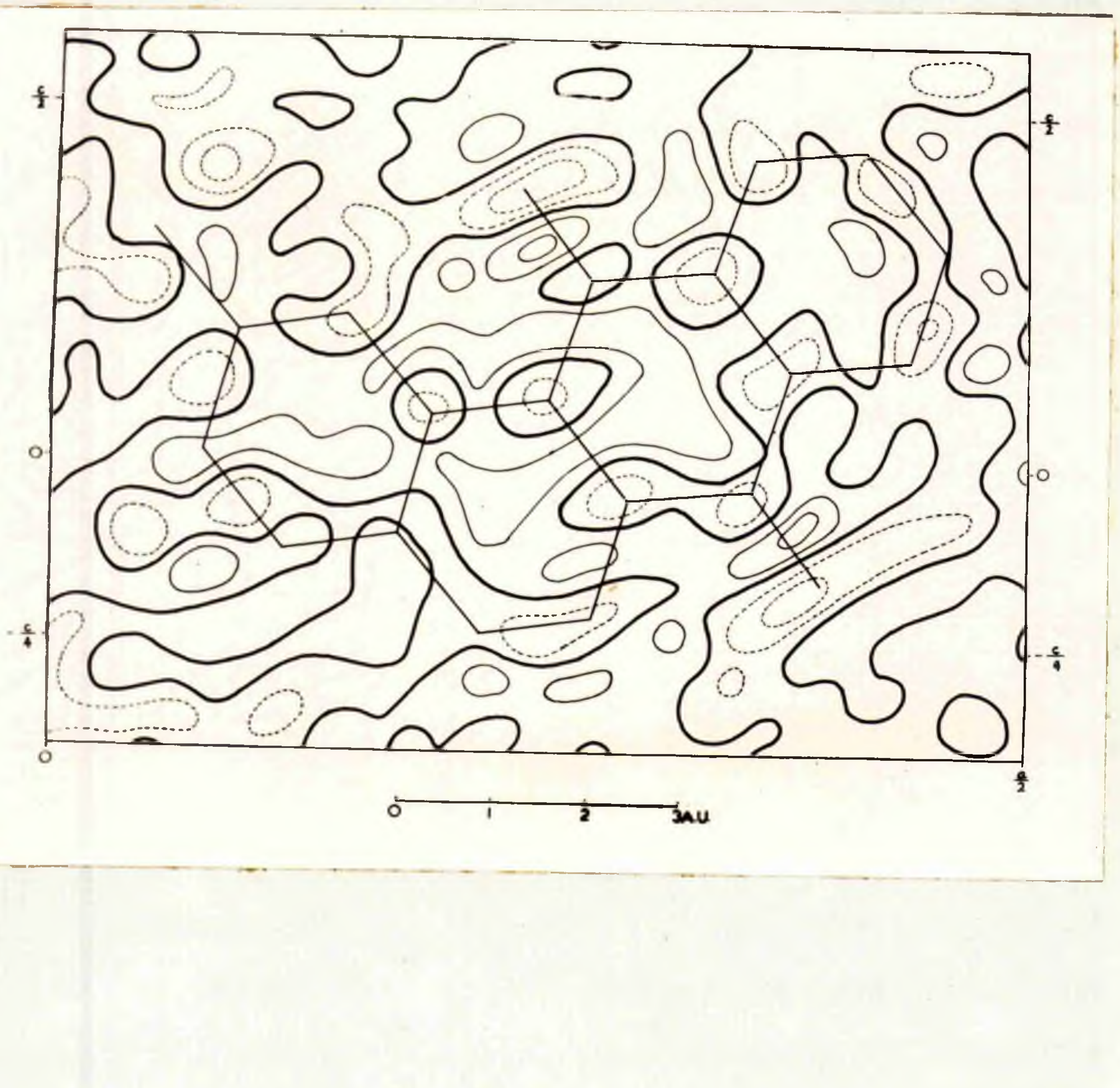


Fig. 4.6. The $(F_e - F_c)$ Fourier projection down the **b** - axis. The contours are at intervals of 0.2 e./A.U.^{2}, the zero contours being the solid black line and the positive contours are dotted.

TABLE 4.4.

TYPE	ATOM	B(A.U.^{2})
Oxygen	B,K.	5.0
Carbon	A,C,I,J,L,M,R,U.	4.0
Carbon	D,F,G,H,N,O,P,Q,S,T.	4.5
Carbon	E.	5.0
Hydrogen	$D',F',G',H',N',P',Q',S',T',E_1',E_2',E_3'$.	6.0

The reliability index was calculated and was found to be R = 0.14 compared with R = 0.18 when the structure factors were calculated without the hydrogen contribution and individual isotropic temperature factors. The least squares cycle was computed and the new co-ordinates obtained are shown in Table 4,5. The structure factors of the (h0l) zone were recalculated and the reliability index dropped to 0.112. The phases of all the observed structure factors were used to compute a difference Fourier synthesis and the resulting map of electron density is shown in Fig. 4,6. The difference Fourier was prepared to enable an estimate to be made of the individual isotropic temperature factors, and one interesting feature of the electron density map was the ellipticity of the contours around the oxygen atom sites, which showed that there was a definite anisotropy in the temperature factors of these atoms. The individual isotropic temperature factors which were used in the initial stage of

TABLE 4.5.

Atomic x and z co-ordinates and individual isotropic temperature factors used in the first cycle of 3-dimensional least squares refinement.

ATOM.	x/a.	z/c.	x(A.U.).	z(A.U.).	B.
B	0.3937	-0.1588	8.139	-1.234	4.6
K	0.2388	0.3845	4.937	2.987	4.4
A	0.3594	-0.0322	7.430	-0.250	3.6
C	0.3783	0.1324	7.821	1.028	3.6
D	0.4382	0.1509	9.059	1.172	4.1
E	0.0498	0.3209	1.030	2.493	5.2
F	0.4556	0.3056	9.419	2.374	4.5
G	0.4151	0.4453	8.581	3.459	4.2
H	0.3560	0.4287	7.360	3.330	3.9
I	0.3372	0.2727	6.971	2.118	3.6
J	0.2734	0.2556	5.652	1.986	3.7
L	0.2538	0.0912	5.247	0.708	3.5
M	0.1951	0.0681	4.033	0.529	3.7
N	0.1502	0.2044	3.105	1.588	4.0
O	0.0947	0.1757	1.958	1.365	4.5
P	0.0786	0.0096	1.625	0.075	4.9
Q	0.1193	-0.1226	2.466	-0.952	4.7
R	0.1778	-0.0984	3.676	-0.764	4.1
S	0.2199	-0.2382	4.546	-1.850	4.4
T	0.2774	-0.2104	5.735	-1.634	4.2
U	0.2949	-0.0481	6.096	-0.374	3.7

the three-dimensional least squares refinement were extracted from the electron density map by the method outlined in Chapter 3, section (d) and these are given in Table 4,6 below.

TABLE 4.6.

The individual isotropic temperature factors used in the first cycle of the three-dimensional least squares refinement.

ATOM	B (A.U.^{2})	ATOM	B (A.U.^{2})	ATOM	B (A.U.^{2})
B	4.6	G	4.2	O	4.5
K	4.4	H	3.9	P	4.9
A	3.6	I	3.6	Q	4.7
C	3.6	J	3.7	R	4.1
D	4.1	L	3.5	S	4.4
E	5.2	M	3.7	T	4.2
F	4.5	N	4.0	U	3.7

The subsequent refinement of 2'-methyl 1:2-benzanthraquinone was carried out by the method of three-dimensional least squares on the Deuce computer in the University of Glasgow. The least squares programme, which was devised by Dr. J.S. Rollett, refines three positional parameters and six anisotropic vibrational parameters for each atom and one overall scale factor for the observed structure factors. Only the parameters of the oxygen and carbon atoms were allowed to change, the contributions of the hydrogen atoms to the calculated structure factors remaining the same in each cycle. The anisotropic thermal motion of the atoms was obtained by assuming that the stationary scattering factor was multiplied by a term

$$\exp.-(b_{11}\,h^2 + b_{22}\,k^2 + b_{33}\,l^2 + b_{12}\,hk + b_{13}\,hl + b_{23}\,kl)$$

depending on the six parameters b_{ij} which are refined by the programme. The output of the least squares programme gave the new set of co-ordinates and the new values of b_{ij} to be used in the next cycle. Data was also obtained which enabled an estimate to be made of the standard deviations of the co-ordinates used in the cycle.

The co-ordinates used in the initial cycle were the x and z co-ordinates given in Table 4,5 and the y co-ordinates given in Table 4,3. The individual isotropic temperature factors used were those given in Table 4,6. As there was some doubt as to whether the structure factors of the layer lines of the b - axis were on the same scale, the smaller structure factors of all but the 3rd layer line were omitted in the first cycle and only half-shifts were permitted in the co-ordinates. When the structure factors of the individual layer lines were rescaled to the values of the calculated structure factors, a further cycle of least squares was computed using all the 863 observed structure factors of the zero, first, second and third layer lines of the b - axis and the reliability index was found to be 0.17. The final set of co-ordinates derived from this cycle are given in Table 4,7 and the values of b_{ij} obtained were converted to values of U_{ij} (Chap. III sect. (d)) and those are shown in Table 4,8. The atomic co-ordinates of all the hydrogen atoms except those of the methyl group were recalculated from the final set of carbon co-ordinates assuming a C - H bond length of 1.05 A.U., and the estimated co-ordinates of all the hydrogen atoms are given in Table 4,9.

The final set of observed and calculated structure factors are given in Table 4,10 along with the values of $\Delta F = F_o - F_c$ and the phase angle α of each observed reflection. The maximum estimated value of the structure factors of the unobserved reflections are also given in Table 4,10.

TABLE 4.7.

The final carbon and oxygen atomic co-ordinates.

ATOM	x(A.U.)	y(A.U.)	z(A.U.)	
B	8.1199	-0.2654	-1.2327	O1
K	4.9332	0.1829	2.9867	O2
A	7.4284	-0.2093	-0.2459	A
C	7.8181	-0.7377	0.9720	B
D	9.0327	-1.4373	1.1466	C
E	1.0134	2.5068	2.4677	T
F	9.4261	-1.8840	2.4247	D
G	8.6025	-1.7816	3.5102	E
H	7.3306	-1.1532	3.3558	F
I	6.9760	-0.6291	2.0975	G
J	5.6190	0.0670	1.9338	H
L	5.2684	0.7103	0.7345	I
M	4.0182	1.4452	0.5588	J
N	3.0744	1.6625	1.5454	K
O	1.9578	2.3136	1.3882	L
P	1.6618	2.8144	0.0764	M
Q	2.4240	2.6074	-0.9940	N
R	3.7050	1.9503	-0.7656	P
S	4.5663	1.7282	-1.8865	Q
T	5.6953	1.0210	-1.7041	R
U	6.1069	0.5148	-0.3599	S

TABLE 4.8.

The values of U_{ij} derived from the last cycle of least squares refinement.

(Values in 10^{-2} A.U.^{2})

ATOM	U_{11}	U_{22}	U_{33}	U_{13}	U_{12}	U_{23}
B	5.82	5.82	6.22	1.95	0.00	0.00
K	5.57	5.57	6.34	0.09	0.00	0.00
A	4.57	4.57	4.55	0.07	0.00	0.00
C	4.57	4.57	4.55	0.07	0.00	0.00
D	5.20	5.20	5.82	0.08	0.00	0.00
E	6.59	6.59	7.75	0.10	0.00	0.00
F	5.71	5.71	6.54	0.09	0.00	0.00
G	5.32	5.32	5.31	0.08	0.00	0.00
H	4.94	4.94	4.93	0.08	0.00	0.00
I	4.57	4.57	5.06	0.07	0.00	0.00
J	4.68	4.68	4.11	0.07	0.00	0.00
L	4.43	4.43	4.43	0.07	0.00	0.00
M	4.68	4.68	5.24	0.07	0.00	0.00
N	5.07	5.07	5.06	0.08	0.00	0.00
O	5.70	5.70	7.31	0.09	0.00	0.00
P	6.20	6.20	3.97	0.10	0.00	0.00
Q	5.95	5.95	6.83	0.09	0.00	0.00
R	5.20	5.20	5.92	0.08	0.00	0.00
S	5.57	5.57	6.32	0.09	0.00	0.00
T	5.32	5.32	6.66	0.08	0.00	0.00
U	4.68	4.68	4.68	0.07	0.00	0.00

TABLE 4.9.

The calculated hydrogen atomic co-ordinates.

ATOM	x(A.U.)	y(A.U.)	z(A.U.)
D'	9.671	-1.544	0.318
F'	10.355	-2.360	2.549
G'	8.891	-2.410	4.444
H'	6.692	-1.046	4.180
N'	3.319	1.307	2.501
P'	0.769	3.333	-0.107
Q'	2.179	2.963	-1.950
S'	4.313	2.100	-2.836
T'	6.313	0.865	-2.538
E_1'	0.062	2.452	4.692
E_2'	1.158	2.923	3.053
E_3'	1.158	1.981	3.053

TABLE 4,10.

THE OBSERVED AND CALCULATED STRUCTURE FACTORS OF 2'-METHYL 1:2-BENZANTHRAQUINONE.

h	k	l	F_o	F_c	ΔF	α°
1	0	0	18.8	18.6	0.2	180.0
2			40.0	44.3	−4.3	180.0
3			11.4	11.6	−0.2	0.0
4			21.0	18.8	2.2	180.0
5			11.3	10.1	1.2	0.0
6			36.0	34.4	1.6	180.0
7			8.6	8.1	0.5	180.0
8			5.7	5.2	0.5	0.0
9			7.3	6.6	0.7	180.0
10			11.4	10.5	0.9	180.0
11			16.1	14.5	1.6	0.0
12			2.3	2.7	−0.4	180.0
13			3.4	3.6	−0.2	180.0
14			2.2	1.4	0.8	0.0
15			1.6	0.7	0.9	180.0
16			2.0	2.5	−0.5	180.0
17			< 1.3			
18			< 1.4			
19			3.9	4.2	−0.3	180.0
20			2.7	2.9	−0.2	0.0
21			2.2	2.1	0.1	0.0
22			< 1.3			
23			< 1.3			
24			< 1.2			
25			< 1.1			
26			< 0.9			
0	0	1	51.6	54.8	−3.2	0.0
1			13.7	12.5	1.2	180.0
2			12.4	10.4	2.0	180.0
3			33.5	35.5	−2.0	180.0
4			25.9	28.0	−2.1	180.0
5			27.2	27.1	0.1	180.0
6			5.8	6.0	−0.2	0.0
7			11.7	12.2	−0.5	180.0
8			8.7	10.0	−1.3	0.0
9			21.6	21.4	0.2	180.0
10			16.9	15.9	1.0	0.0
11			44.6	44.3	0.3	0.0
12			14.2	14.3	−0.1	180.0
13			< 1.1			
14			5.2	3.4	1.8	180.0
15			< 1.1			
16			2.3	3.4	−1.1	0.0
17			5.2	6.7	−1.5	180.0
18			3.9	4.1	−0.2	0.0
19			1.8	3.3	−1.5	0.0
20			2.0	2.6	−0.6	0.0
21			1.5	2.0	−0.5	180.0
22			7.3	7.9	−0.6	180.0
23			2.0	2.2	−0.2	0.0
24			< 1.2			
25			< 1.0			

h	k	l	F_o	F_c	ΔF	α°
26	0	1	< 0.8			
0	0	2	17.6	15.7	1.9	180.0
1			26.0	24.1	1.9	0.0
2			7.0	8.4	−1.4	180.0
3			11.3	12.4	−1.1	0.0
4			5.1	5.8	−0.7	180.0
5			9.7	9.6	0.1	0.0
6			8.8	9.8	−1.0	0.0
7			15.0	15.7	−0.7	180.0
8			1.2	3.4	−2.2	0.0
9			5.2	6.3	−1.1	0.0
10			9.8	8.4	1.4	0.0
11			6.8	6.3	0.5	0.0
12			< 1.1			
13			2.3	0.5	1.8	180.0
14			3.4	3.8	−0.4	180.0
15			5.8	7.6	−1.8	180.0
16			2.9	1.2	1.7	180.0
17			2.6	2.8	−0.2	0.0
18			4.2	0.9	3.3	180.0
19			< 1.5			
20			2.6	3.0	−0.4	0.0
21			4.9	5.3	−0.4	180.0
22			2.7	3.6	−0.9	180.0
23			< 1.2			
24			< 1.1			
25			1.2	1.4	−0.2	0.0
26			< 0.7			
0	0	3	8.2	9.2	−1.0	180.0
1			< 1.4			
2			5.3	7.5	−2.2	0.0
3			22.7	22.0	0.7	0.0
4			41.5	39.9	1.6	0.0
5			34.8	33.8	1.0	180.0
6			11.7	13.2	−1.5	180.0
7			3.2	2.0	1.2	0.0
8			2.6	2.5	0.1	180.0
9			3.4	3.5	−0.1	0.0
10			15.0	16.1	−1.1	180.0
11			3.7	3.5	0.2	0.0
12			2.0	0.8	1.2	0.0
13			< 1.3			
14			< 1.3			
15			1.7	0.0	1.7	180.0
16			< 1.4			
17			2.0	0.1	1.9	180.0
18			< 1.8			
19			< 1.4			
20			< 1.4			
21			2.0	1.8	0.2	180.0
22			< 1.3			
23			< 1.2			

h	k	l	F_o	F_c	ΔF	α°
24	0	3	2.3	3.0	0.7	0.0
25			< 0.8			
0	0	4	7.1	8.0	−0.9	180.0
1			3.4	3.7	−0.3	0.0
2			4.3	4.3	0.0	180.0
3			20.0	18.3	1.7	0.0
4			7.7	7.7	0.0	0.0
5			30.3	29.0	1.3	180.0
6			4.1	3.5	0.6	0.0
7			2.1	3.6	−1.5	180.0
8			8.7	8.0	0.7	180.0
9			1.7	0.7	1.0	180.0
10			2.7	3.2	−0.5	0.0
11			1.9	1.9	0.0	180.0
12			3.3	2.2	1.1	0.0
13			3.2	4.2	−1.0	180.0
14			18.0	19.6	−1.6	0.0
15			12.4	13.3	−0.9	0.0
16			19.5	20.7	−1.2	180.0
17			< 1.4			
18			< 1.4			
19			< 1.4			
20			< 1.3			
21			< 1.3			
22			< 1.2			
23			< 1.1			
24			< 1.0			
0	0	5	2.3	1.0	1.3	0.0
1			1.8	1.4	0.4	0.0
2			< 1.1			
3			< 1.2			
4			< 1.2			
5			4.3	4.6	0.3	0.0
6			9.7	9.7	0.0	180.0
7			< 1.3			
8			< 1.3			
9			1.9	1.0	0.9	0.0
10			< 1.3			
11			< 1.4			
12			< 1.4			
13			< 1.4			
14			19.2	18.8	0.4	0.0
15			4.4	3.8	0.6	180.0
16			9.8	10.6	−0.8	180.0
17			< 1.3			
18			3.4	4.7	−1.3	180.0
19			< 1.3			
20			2.8	0.7	2.1	180.0
21			< 1.1			
22			< 0.9			
23			< 0.6			
0	0	6	6.0	4.6	1.4	180.0

h	k	l	F_o	F_c	ΔF	α°
1	0	6	4.8	6.0	−1.2	0.0
2			< 1.3			
3			1.5	2.8	−1.3	0.0
4			2.3	3.8	−1.5	180.0
5			< 1.3			
6			3.0	3.2	−0.2	180.0
7			3.6	4.0	−0.4	0.0
8			< 1.4			
9			< 1.4			
10			< 1.3			
11			1.7	0.0	1.7	180.0
12			1.9	2.8	−0.9	0.0
13			1.5	0.5	1.0	0.0
14			< 1.4			
15			< 1.3			
16			< 1.3			
17			4.5	4.8	−0.3	180.0
18			2.6	0.4	2.2	0.0
19			< 1.2			
20			< 0.9			
21			< 0.7			
0	0	7	1.9	5.2	−3.3	0.0
1			2.9	3.0	−0.1	180.0
2			1.9	1.9	0.0	180.0
3			< 1.6			
4			3.1	4.6	−1.5	180.0
5			< 1.4			
6			< 1.4			
7			6.4	7.9	−1.5	180.0
8			3.1	2.5	0.6	0.0
9			6.8	7.3	−0.5	0.0
10			3.2	3.9	−0.7	180.0
11			< 1.4			
12			< 1.4			
13			< 1.4			
14			< 1.3			
15			< 1.2			
16			< 1.1			
17			< 1.0			
18			< 0.8			
19			< 0.7			
0	0	8	< 1.6			
1			< 1.6			
2			3.4	3.6	−0.2	180.0
3			1.6	0.6	1.0	0.0
4			1.7	0.8	0.9	0.0
5			1.2	1.9	−0.7	180.0
6			2.3	0.3	2.0	0.0
7			2.9	3.4	−0.5	180.0
8			5.6	6.1	−0.5	0.0
9			2.1	2.5	−0.4	0.0
10			< 1.3			
11			< 1.2			
12			< 1.1			
13			< 1.1			
14			< 0.9			
15			< 0.8			
16			< 0.6			
0	0	9	< 1.2			
1			3.9	3.6	0.3	0.0
2			2.6	2.1	0.5	0.0

h	k	l	F_o	F_c	ΔF	α°
3	0	9	< 1.2			
4			< 1.2			
5			< 1.1			
6			< 1.1			
7			< 1.1			
8			1.4	1.0	0.4	180.0
9			< 1.0			
10			< 0.8			
11			< 0.7			
0	0	10	< 0.6			
1			3.4	4.7	−1.3	0.0
2			< 0.7			
$\bar{1}$	0	1	61.1	61.9	−0.8	0.0
$\bar{2}$			22.5	23.6	−1.1	180.0
$\bar{3}$			14.3	14.6	−0.3	0.0
$\bar{4}$			16.0	16.8	−0.8	180.0
$\bar{5}$			12.7	12.6	0.1	0.0
$\bar{6}$			5.7	7.5	−1.8	180.0
$\bar{7}$			14.3	13.7	0.6	0.0
$\bar{8}$			11.2	9.4	1.8	180.0
$\bar{9}$			4.5	3.1	1.4	0.0
$\bar{10}$			14.4	15.8	−1.4	0.0
$\bar{11}$			6.7	4.3	2.4	180.0
$\bar{12}$			2.2	2.5	−0.3	180.0
$\bar{13}$			2.6	3.4	0.8	0.0
$\bar{14}$			1.7	2.0	−0.3	0.0
$\bar{15}$			1.6	1.5	0.1	180.0
$\bar{16}$			8.8	8.7	0.1	0.0
$\bar{17}$			4.9	5.3	−0.4	180.0
$\bar{18}$			7.4	6.4	1.0	180.0
$\bar{19}$			7.3	8.5	−1.2	180.0
$\bar{20}$			2.1	3.4	−1.3	180.0
$\bar{21}$			2.2	2.4	−0.2	0.0
$\bar{22}$			2.4	2.4	0.0	0.0
$\bar{23}$			2.4	2.1	0.3	0.0
$\bar{24}$			< 1.2			
$\bar{25}$			< 1.1			
$\bar{26}$			< 0.9			
$\bar{1}$	0	2	31.6	29.5	1.1	180.0
$\bar{2}$			15.4	15.5	−0.1	0.0
$\bar{3}$			4.7	4.7	0.0	0.0
$\bar{4}$			20.8	21.0	−0.2	180.0
$\bar{5}$			7.5	6.4	1.1	0.0
$\bar{6}$			6.8	6.7	0.1	180.0
$\bar{7}$			12.5	12.9	−0.4	180.0
$\bar{8}$			12.7	10.7	2.0	180.0
$\bar{9}$			8.9	7.8	1.1	180.0
$\bar{10}$			2.6	0.8	1.8	0.0
$\bar{11}$			2.0	1.1	0.9	0.0
$\bar{12}$			12.2	11.4	0.8	0.0
$\bar{13}$			3.7	3.7	0.0	180.0
$\bar{14}$			8.8	9.3	−0.5	0.0
$\bar{15}$			5.6	5.7	−0.1	180.0
$\bar{16}$			18.4	18.7	−0.3	0.0
$\bar{17}$			15.7	15.8	−0.1	0.0
$\bar{18}$			27.1	27.1	0.0	180.0
$\bar{19}$			2.0	2.2	−0.2	180.0
$\bar{20}$			< 1.4			
$\bar{21}$			< 1.3			
$\bar{22}$			< 1.3			
$\bar{23}$			< 1.2			

h	k	l	F_o	F_c	ΔF	α°
$\bar{24}$	0	2	2.2	2.5	−0.3	0.0
$\bar{25}$			< 1.0			
$\bar{26}$			< 0.8			
$\bar{1}$	0	3	21.9	21.1	0.8	0.0
$\bar{2}$			7.3	5.3	2.0	180.0
$\bar{3}$			5.1	1.6	3.5	180.0
$\bar{4}$			15.1	12.1	3.0	0.0
$\bar{5}$			11.8	11.0	0.8	0.0
$\bar{6}$			33.9	31.0	2.9	0.0
$\bar{7}$			37.9	34.7	3.2	180.0
$\bar{8}$			22.5	20.9	1.6	180.0
$\bar{9}$			7.6	6.1	1.5	0.0
$\bar{10}$			8.4	6.3	2.1	180.0
$\bar{11}$			2.6	3.8	−1.2	180.0
$\bar{12}$			3.4	4.1	−0.7	180.0
$\bar{13}$			< 1.3			
$\bar{14}$			4.6	3.8	0.8	0.0
$\bar{15}$			2.3	0.1	2.2	180.0
$\bar{16}$			< 1.4			
$\bar{17}$			15.0	12.5	2.5	0.0
$\bar{18}$			5.6	7.0	−1.4	180.0
$\bar{19}$			4.5	4.5	0.0	180.0
$\bar{20}$			2.2	2.7	−0.5	0.0
$\bar{21}$						
$\bar{22}$			2.6	1.8	0.8	0.0
$\bar{23}$			2.2	1.8	0.4	180.0
$\bar{24}$			< 1.4			
$\bar{25}$			< 1.1			
$\bar{1}$	0	4	< 1.0			
$\bar{2}$			3.0	3.7	−0.7	180.0
$\bar{3}$			2.0	4.7	−2.7	0.0
$\bar{4}$			3.2	4.3	−1.1	0.0
$\bar{5}$			< 1.0			
$\bar{6}$			16.1	13.9	2.2	0.0
$\bar{7}$			2.6	2.2	0.4	0.0
$\bar{8}$			8.8	7.1	1.7	180.0
$\bar{9}$			2.5	2.0	0.5	0.0
$\bar{10}$			2.7	4.0	−1.3	180.0
$\bar{11}$			9.0	8.2	0.8	0.0
$\bar{12}$			3.5	1.9	1.6	180.0
$\bar{13}$			< 1.3			0.0
$\bar{14}$			2.6	4.8	−2.2	0.0
$\bar{15}$			3.2	3.8	−0.6	180.0
$\bar{16}$			< 1.4			
$\bar{17}$			4.9	5.3	−0.4	180.0
$\bar{18}$			< 1.4			
$\bar{19}$			4.3	4.5	−0.2	0.0
$\bar{20}$			2.6	2.7	−0.1	180.0
$\bar{21}$			2.0	1.9	0.1	180.0
$\bar{22}$			2.8	2.5	0.3	0.0
$\bar{23}$			2.1	1.9	0.2	180.0
$\bar{24}$			< 0.9			
$\bar{1}$	0	5	1.7	4.0	−2.3	0.0
$\bar{2}$			5.7	6.1	−0.4	180.0
$\bar{3}$			6.7	5.2	1.5	0.0
$\bar{4}$			4.6	5.0	−0.4	180.0
$\bar{5}$			9.9	10.2	−0.3	180.0
$\bar{6}$			6.3	5.4	0.9	180.0
$\bar{7}$			4.9	4.9	0.0	180.0
$\bar{8}$			12.2	9.7	2.5	0.0
$\bar{9}$			1.8	2.4	−0.6	180.0

h	k	l	F_o	F_c	ΔF	α°
$\bar{10}$	0	5	1.8	0.6	1.2	180.0
$\bar{11}$			< 1.3			
$\bar{12}$			2.8	6.5	−3.7	0.0
$\bar{13}$			13.4	12.7	0.7	0.0
$\bar{14}$			2.9	2.5	0.4	180.0
$\bar{15}$			4.0	3.0	1.0	180.0
$\bar{16}$			1.6	1.8	−0.2	180.0
$\bar{17}$			1.6	0.2	1.4	180.0
$\bar{18}$			< 1.3			
$\bar{19}$			< 1.3			
$\bar{20}$			< 1.3			
$\bar{21}$			< 1.1			
$\bar{22}$			< 1.0			
$\bar{1}$	0	6	4.7	3.6	1.1	180.0
$\bar{2}$			33.0	34.8	−1.8	0.0
$\bar{3}$			< 1.2			
$\bar{4}$			16.6	14.3	2.3	180.0
$\bar{5}$			2.5	5.1	−2.6	180.0
$\bar{6}$			2.7	2.8	−0.1	180.0
$\bar{7}$			1.7	2.0	−0.3	180.0
$\bar{8}$			2.9	2.2	0.7	180.0
$\bar{9}$			2.5	3.0	−0.5	180.0
$\bar{10}$			6.3	4.0	2.3	0.0
$\bar{11}$			3.4	0.9	2.5	180.0
$\bar{12}$			8.4	7.5	0.9	0.0
$\bar{13}$			12.5	12.4	0.1	180.0
$\bar{14}$			< 1.4			
$\bar{15}$			4.0	5.0	−1.0	180.0
$\bar{16}$			< 1.3			
$\bar{17}$			< 1.3			
$\bar{18}$			2.4	1.8	0.6	0.0
$\bar{19}$			1.5	0.7	0.8	180.0
$\bar{20}$			< 1.0			
$\bar{1}$	0	7	12.2	10.4	1.8	180.0
$\bar{2}$			19.1	19.1	0.0	0.0
$\bar{3}$			13.8	12.7	1.1	0.0
$\bar{4}$			15.0	14.1	0.9	180.0
$\bar{5}$			< 1.4			
$\bar{6}$			2.0	3.7	−1.7	180.0
$\bar{7}$			3.5	2.7	0.8	0.0
$\bar{8}$			< 1.4			
$\bar{9}$			2.4	1.0	1.4	180.0
$\bar{10}$			3.0	1.2	1.8	0.0
$\bar{11}$			< 1.4			
$\bar{12}$			< 1.4			
$\bar{13}$			< 1.4			
$\bar{14}$			< 1.4			
$\bar{15}$			< 1.3			
$\bar{16}$			< 1.3			
$\bar{17}$			1.8	1.1	0.7	180.0
$\bar{18}$			< 1.1			
$\bar{19}$			< 0.8			
$\bar{1}$	0	8	2.9	2.2	0.7	0.0
$\bar{2}$			< 1.3			
$\bar{3}$			2.4	0.2	2.2	180.0
$\bar{4}$			2.7	0.7	2.0	0.0
$\bar{5}$			2.5	1.9	0.6	0.0
$\bar{6}$			4.8	4.3	0.5	180.0
$\bar{7}$			< 1.3			
$\bar{8}$			< 1.3			
$\bar{9}$			< 1.3			

h	k	l	F_o	F_c	ΔF	α°
$\bar{10}$	0	8	< 1.3			
$\bar{11}$			3.1	1.7	1.4	180.0
$\bar{12}$			4.4	2.6	1.8	0.0
$\bar{13}$			< 1.1			
$\bar{14}$			< 1.0			
$\bar{15}$			< 0.9			
$\bar{1}$	0	9	< 1.2			
$\bar{2}$			< 1.2			
$\bar{3}$			2.9	1.4	1.5	180.0
$\bar{4}$			< 1.2			
$\bar{5}$			1.2	−2.0	−0.8	0.0
$\bar{6}$			1.1	−1.5	−0.4	180.0
$\bar{7}$			< 1.1			
$\bar{8}$			2.3	2.3	0.0	0.0
$\bar{9}$			3.1	3.3	−0.2	180.0
$\bar{10}$			2.7	2.1	0.6	180.0
$\bar{11}$			< 0.8			
$\bar{12}$			< 0.6			
$\bar{1}$	0	10	< 0.7			
$\bar{2}$			< 0.7			
$\bar{3}$			< 0.7			
$\bar{4}$			< 0.7			
1	1	0	2.2	5.5	−3.3	170.8
2			53.1	60.4	−7.3	247.0
3			82.0	88.7	−6.7	332.8
4			41.8	37.3	4.5	66.6
5			13.1	19.4	−6.3	216.0
6			20.7	18.5	2.2	31.4
7			27.7	27.8	−0.1	266.1
8			24.8	19.9	4.9	26.0
9			19.7	19.6	0.1	88.0
10			9.1	9.0	0.1	295.5
11			6.5	2.7	3.8	133.3
12			6.0	5.2	0.8	297.8
13			3.5	3.5	0.0	112.6
14			< 3.0			
15			< 3.2			
16			< 3.3			
17			< 3.4			
18			< 3.4			
19			4.2	3.3	0.9	36.6
20			< 3.3			
21			< 3.2			
22			< 3.0			
23			< 2.6			
24			< 2.4			
25			< 1.8			
0	1	1	28.2	19.9	8.3	336.8
1			27.9	25.2	2.7	168.3
2			78.5	89.3	−10.8	279.1
3			53.5	52.1	1.4	20.7
4			34.1	29.7	4.4	86.3
5			3.8	4.2	−0.4	237.3
6			8.2	8.8	−0.6	90.8
7			24.3	22.1	2.2	218.3
8			27.1	30.0	−2.9	129.9
9			9.8	10.5	−0.7	75.7
10			6.4	5.2	1.2	247.0
11			8.0	6.3	1.7	34.5
12			7.8	7.3	0.5	169.4
13			12.8	11.8	1.0	358.9

h	k	l	F_o	F_c	ΔF	α°
14	1	1	13.2	13.2	0.0	353.3
15			6.4	6.5	−0.1	102.2
16			3.6	1.1	2.5	282.3
17			< 3.0			
18			3.4	4.1	−0.7	36.3
19			4.7	6.4	−1.7	328.3
20			3.5	5.3	−1.8	278.3
21			< 3.2			
22			< 3.0			
23			< 2.7			
24			< 2.4			
25			< 1.0			
0	1	2	12.7	13.3	−0.6	222.4
1			10.2	10.6	−0.4	113.0
2			21.8	21.5	0.3	80.8
3			6.6	5.5	1.1	299.5
4			6.5	12.9	−6.4	353.4
5			3.5	6.4	−2.9	154.0
6			8.6	11.1	−2.5	138.2
7			8.3	7.7	0.6	100.6
8			15.9	15.4	0.5	263.5
9			7.5	6.6	0.9	66.0
10			< 2.6			
11			6.4	3.0	3.4	61.3
12			8.1	6.5	1.6	262.3
13			14.0	15.0	−1.0	284.4
14			9.5	8.4	1.1	61.9
15			3.8	2.4	1.4	62.5
16			< 2.6			
17			3.9	3.9	0.0	130.1
18			< 3.4			
19			< 3.4			
20			< 3.3			
21			< 3.1			
22			< 2.9			
23			2.6	2.2	0.4	39.7
24			3.5	3.3	0.2	111.8
25			2.1	2.5	−0.4	109.0
0	1	3	9.0	9.8	−0.8	118.0
1			26.3	26.5	−0.2	117.9
2			24.3	28.6	−4.3	20.6
3			22.2	21.8	0.4	269.8
4			6.2	5.8	0.4	153.8
5			9.9	9.1	0.8	308.3
6			9.6	9.7	−0.1	300.0
7			9.0	11.1	−2.1	356.0
8			3.7	3.5	0.2	118.9
9			3.5	3.2	0.3	172.3
10			3.0	3.0	0.0	208.5
11			8.3	8.4	−0.1	234.8
12			8.8	10.5	−1.7	108.5
13			8.4	7.8	0.6	58.4
14			7.6	7.5	0.1	288.1
15			3.3	2.8	0.5	120.8
16			< 3.4			
17			< 3.4			
18			< 3.4			
19			< 3.3			
20			< 3.1			
21			< 2.9			
22			< 2.7			

h	k	l	F_o	F_c	ΔF	α°
23	1	3	< 2.4			
24			< 2.0			
0	1	4	8.3	5.5	2.8	149.4
1			< 2.5			
2			9.2	10.0	0.8	11.0
3			< 2.6			
4			5.6	6.7	1.1	290.6
5			6.6	4.6	2.0	264.2
6			15.6	14.3	1.3	298.5
7			17.8	17.3	0.5	68.3
8			10.5	10.3	0.2	140.1
9			8.3	6.1	2.2	238.4
10			< 3.1			
11			13.2	15.7	2.5	193.0
12			18.0	21.4	3.4	96.8
13			11.8'	14.4	2.6	347.4
14			6.9	8.0	1.1	246.3
15			< 3.4			
16			3.2	4.4	1.2	259.8
17			3.9	4.3	0.4	310.6
18			4.0	4.6	0.6	11.9
19			4.3	5.1	0.8	160.4
20			< 2.8			
21			< 2.4			
22			< 2.0			
23			< 1.6			
0	1	5	3.1	5.3	2.2	38.5
1			3.4	5.3	1.9	144.3
2			2.9	3.4	0.5	156.2
3			5.6	5.8	0.2	345.7
4			3.6	3.9	0.3	234.8
5			3.4	2.6	0.8	135.6
6			6.1	5.4	0.7	338.8
7			5.0	4.2	0.8	88.9
8			3.2	2.3	0.9	251.0
9			< 3.3			
10			< 3.4			
11			4.9	4.7	0.2	162.2
12			3.7	4.0	0.3	33.0
13			< 3.4			
14			3.5	2.6	0.9	314.1
15			< 3.3			
16			6.6	7.1	0.5	237.3
17			8.1	8.4	0.3	330.3
18			9.2	9.3	0.1	83.4
19			4.5	4.8	0.3	187.0
20			< 2.3			
21			< 1.9			
22			< 1.4			
0	1	6	3.4	4.7	1.3	222.5
1			10.0	10.6	0.6	335.1
2			< 3.3			
3			< 3.3			
4			< 3.4			
5			< 3.4			
6			< 3.4			
7			< 3.4			
8			< 3.6			
9			3.4	4.5	1.1	172.9
10			< 3.4			
11			< 3.4			

h	k	l	F_o	F_c	ΔF	α°
12	1	6	< 3.[illegible]			
13			< 3.[illegible]			
14			< 3.1			
15			< 3.0			
16			2.9	1.6	1.3	295.2
17			3.7	2.4	1.3	30.6
18			< 2.3			
19			< 2.0			
20			< 1.8			
0	1	7	14.3	16.6	2.3	280.4
1			12.2	12.4	0.2	11.9
2			7.0	5.7	1.3	130.6
3			< 3.4			
4			< 3.4			
5			6.0	6.7	0.7	215.3
6			6.1	7.9	1.8	116.3
7			< 3.3			
8			< 3.3			
9			< 3.2			
10			< 3.2			
11			< 3.1			
12			< 2.9			
13			< 2.8			
14			< 2.6			
15			< 2.4			
16			3.4	3.0	0.4	55.6
17			2.7	2.5	0.2	309.7
18			< 0.9			
0	1	8	< 3.2			
1			< 3.2			
2			< 3.1			
3			< 3.1			
4			< 3.1			
5			< 3.1			
6			< 3.0			
7			< 2.9			
8			< 2.8			
9			< 2.7			
10			2.9	3.0	0.1	218.9
11			4.1	4.1	0.0	299.5
12			< 2.2			
13			< 2.0			
14			< 1.7			
0	1	9	< 2.5			
1			4.7	2.7	2.0	283.7
2			< 2.4			
3			< 2.3			
4			< 2.3			
5			< 2.2			
6			< 2.1			
7			< 2.0			
8			< 1.8			
9			< 1.6			
10			< 1.1			
$\bar{1}$	1	1	11.4	7.9	3.5	103.5
$\bar{2}$			4.2	3.3	0.9	237.5
$\bar{3}$			15.8	12.9	2.9	263.4
$\bar{4}$			17.9	12.3	5.6	68.8
$\bar{5}$			5.3	8.0	2.7	171.3
$\bar{6}$			7.7	4.6	3.1	278.7
$\bar{7}$			8.0	10.3	2.3	341.9

h	k	l	F_o	F_c	ΔF	α°
$\bar{8}$	1	1	6.7	6.1	0.6	190.2
$\bar{9}$			4.4	3.0	1.4	38.7
$\bar{10}$			4.0	3.7	0.3	158.4
$\bar{11}$			7.2	7.6	0.4	313.1
$\bar{12}$			5.5	6.1	0.6	75.0
$\bar{13}$			2.9	4.8	1.9	178.7
$\bar{14}$			4.2	3.8	0.4	127.0
$\bar{15}$			3.4	2.5	0.9	204.4
$\bar{16}$			7.7	6.7	1.0	151.3
$\bar{17}$			3.6	4.2	0.6	98.6
$\bar{18}$			9.0	6.2	2.8	32.3
$\bar{19}$			8.2	6.2	2.0	150.9
$\bar{20}$			11.8	11.4	0.4	264.6
$\bar{21}$			5.6	3.8	1.8	304.3
$\bar{22}$			3.6	2.5	1.1	5.8
$\bar{23}$			2.7	1.7	1.0	23.6
$\bar{24}$			3.0	1.2	1.8	11.6
$\bar{25}$			2.8	2.1	0.7	247.1
$\bar{1}$	1	2	13.0	11.9	1.1	173.8
$\bar{2}$			< 1.7			
$\bar{3}$			5.1	4.2	0.9	239.2
$\bar{4}$			2.9	6.5	3.6	19.6
$\bar{5}$			5.8	4.7	1.1	241.7
$\bar{6}$			15.9	11.0	4.9	116.2
$\bar{7}$			15.0	8.8	6.2	350.5
$\bar{8}$			8.7	6.4	2.3	143.9
$\bar{9}$			15.5	15.1	0.4	258.2
$\bar{10}$			14.7	10.9	3.8	321.4
$\bar{11}$			10.2	8.4	1.8	4.1
$\bar{12}$			< 2.9			
$\bar{13}$			9.7	11.2	1.5	8.0
$\bar{14}$			12.3	13.2	0.9	278.7
$\bar{15}$			14.2	15.9	1.7	171.9
$\bar{16}$			7.7	7.3	0.4	88.8
$\bar{17}$			5.8	4.9	0.9	122.8
$\bar{18}$			3.7	4.3	0.6	29.4
$\bar{19}$			9.4	7.7	1.7	109.0
$\bar{20}$			8.7	9.0	0.3	218.1
$\bar{21}$			8.5	8.2	0.3	323.7
$\bar{22}$			3.3	3.3	0.0	54.6
$\bar{23}$			< 2.6			
$\bar{24}$			3.3	2.8	0.5	64.8
$\bar{25}$			3.3	3.7	0.4	286.8
$\bar{1}$	1	3	5.2	3.2	2.0	189.6
$\bar{2}$			6.4	3.3	2.1	300.7
$\bar{3}$			14.7	13.2	1.5	325.7
$\bar{4}$			25.3	24.3	1.0	178.9
$\bar{5}$			8.3	9.1	0.8	118.5
$\bar{6}$			8.6	10.9	2.3	60.6
$\bar{7}$			7.1	6.7	0.4	187.9
$\bar{8}$			12.7	12.6	0.1	108.4
$\bar{9}$			9.9	8.5	1.4	184.2
$\bar{10}$			15.7	14.3	1.4	287.4
$\bar{11}$			11.5	10.9	0.6	36.5
$\bar{12}$			< 3.1			
$\bar{13}$			10.7	8.4	2.3	56.5
$\bar{14}$			14.8	14.9	0.1	307.4
$\bar{15}$			14.8	14.0	0.8	285.1
$\bar{16}$			12.4	13.5	1.1	106.5
$\bar{17}$			4.4	3.3	1.1	182.4
$\bar{18}$			< 3.4			

h	k	l	F_o	F_c	ΔF	α°
$\overline{19}$	1	3	< 3.3			
$\overline{20}$			3.9	1.6	2.3	148.1
$\overline{21}$			< 2.9			
$\overline{22}$			< 2.7			
$\overline{23}$			< 2.3			
$\overline{24}$			< 2.0			
$\overline{1}$	1	4	8.3	6.2	2.1	344.8
$\overline{2}$			2.1	0.8	1.3	347.3
$\overline{3}$			9.1	10.0	−0.9	337.0
$\overline{4}$			20.7	20.4	0.3	253.1
$\overline{5}$			14.4	12.1	2.3	118.2
$\overline{6}$			5.5	4.7	0.8	81.6
$\overline{7}$			6.5	4.4	2.1	263.2
$\overline{8}$			3.0	4.2	−1.2	17.3
$\overline{9}$			2.5	2.7	−0.2	185.5
$\overline{10}$			6.8	7.2	−0.4	93.2
$\overline{11}$			2.6	1.6	1.0	301.6
$\overline{12}$			4.3	2.9	1.4	260.5
$\overline{13}$			3.6	1.7	1.9	53.1
$\overline{14}$			3.2	4.0	−0.8	100.8
$\overline{15}$			< 3.4			
$\overline{16}$			3.1	1.9	1.2	193.7
$\overline{17}$			3.5	2.8	0.7	229.6
$\overline{18}$			3.0	0.6	2.4	62.2
$\overline{19}$			2.8	1.9	0.9	341.8
$\overline{20}$			< 2.9			
$\overline{21}$			< 2.6			
$\overline{22}$			< 2.3			
$\overline{23}$			< 2.0			
$\overline{1}$	1	5	3.7	2.4	1.3	261.0
$\overline{2}$			6.3	5.6	0.7	161.5
$\overline{3}$			4.6	4.5	0.1	16.3
$\overline{4}$			8.2	9.4	−1.2	103.7
$\overline{5}$			6.0	6.5	−0.5	224.8
$\overline{6}$			7.9	8.0	−0.1	252.4
$\overline{7}$			2.7	3.4	−0.7	286.4
$\overline{8}$			6.6	5.8	0.8	7.0
$\overline{9}$			5.1	5.5	−0.4	338.4
$\overline{10}$			4.4	4.3	0.1	354.0
$\overline{11}$			< 3.4			
$\overline{12}$			< 3.4			
$\overline{13}$			3.6	3.3	0.3	153.9
$\overline{14}$			3.1	2.9	0.2	217.8
$\overline{15}$			8.9	8.5	0.4	85.1
$\overline{16}$			5.0	4.5	0.5	176.0
$\overline{17}$			5.6	5.5	0.1	273.9
$\overline{18}$			< 3.0			
$\overline{19}$			< 2.8			
$\overline{20}$			< 2.5			
$\overline{21}$			< 2.2			
$\overline{22}$			< 1.7			
$\overline{1}$	1	6	3.4	2.9	0.5	220.7
$\overline{2}$			8.3	8.4	−0.1	128.3
$\overline{3}$			4.4	3.3	1.1	281.8
$\overline{4}$			14.4	15.4	−1.0	67.0
$\overline{5}$			16.0	18.2	−2.2	145.7
$\overline{6}$			15.9	15.7	0.2	252.3
$\overline{7}$			7.0	6.8	0.2	4.1
$\overline{8}$			< 3.4			
$\overline{9}$			6.3	6.5	−0.2	85.4
$\overline{10}$			5.8	7.2	−1.4	305.8
$\overline{11}$			8.2	8.1	0.1	266.0
$\overline{12}$	1	6	4.9	3.2	1.7	117.4
$\overline{13}$			< 3.3			
$\overline{14}$			< 3.2			
$\overline{15}$			3.3	3.7	−0.4	3.3
$\overline{16}$			3.6	2.9	0.7	161.2
$\overline{17}$			< 2.7			
$\overline{18}$			< 2.5			
$\overline{19}$			< 2.2			
$\overline{20}$			< 1.8			
$\overline{1}$	1	7	8.1	8.1	0.0	180.8
$\overline{2}$			5.9	4.8	0.9	60.0
$\overline{3}$			< 3.4			
$\overline{4}$			2.7	3.4	−0.7	16.1
$\overline{5}$			4.2	5.4	−1.2	130.7
$\overline{6}$			4.4	4.9	−0.5	199.4
$\overline{7}$			3.9	3.0	0.9	6.6
$\overline{8}$			5.0	2.0	3.0	272.4
$\overline{9}$			< 3.3			
$\overline{10}$			4.6	3.2	1.4	64.5
$\overline{11}$			3.8	3.7	0.1	289.6
$\overline{12}$			3.0	2.6	0.4	142.9
$\overline{13}$			< 2.9			
$\overline{14}$			< 2.7			
$\overline{15}$			< 2.5			
$\overline{16}$			< 2.3			
$\overline{17}$			< 2.0			
$\overline{18}$			< 1.6			
$\overline{1}$	1	8	4.7	2.4	2.3	210.2
$\overline{2}$			< 3.2			
$\overline{3}$			< 3.1			
$\overline{4}$			< 3.1			
$\overline{5}$			< 3.0			
$\overline{6}$			< 2.9			
$\overline{7}$			< 2.9			
$\overline{8}$			< 2.8			
$\overline{9}$			< 2.6			
$\overline{10}$			< 2.5			
$\overline{11}$			< 2.3			
$\overline{12}$			< 2.1			
$\overline{13}$			< 1.9			
$\overline{14}$			< 1.5			
$\overline{1}$	1	9	6.3	4.2	2.1	97.8
$\overline{2}$			< 2.4			
$\overline{3}$			< 2.4			
$\overline{4}$			< 2.3			
$\overline{5}$			< 2.3			
$\overline{6}$			< 2.2			
$\overline{7}$			< 2.1			
$\overline{8}$			< 2.0			
$\overline{9}$			< 1.8			
$\overline{10}$			< 1.5			
0	2	0	12.6	18.4	−5.8	40.8
1			7.5	9.7	−2.4	117.7
2			11.4	8.7	2.7	85.0
3			14.3	10.0	4.3	173.8
4			9.6	17.7	−8.1	84.6
5			28.0	24.4	3.6	296.8
6			24.4	25.9	−1.5	259.8
7			13.9	11.0	2.9	89.3
8			3.8	3.9	−0.1	244.5
9			5.2	7.3	−2.1	99.5
10			2.5	5.6	−3.1	280.5
11	2	0	4.7	2.5	2.2	130.8
12			2.3	2.9	−0.6	60.5
13			5.2	4.3	0.9	318.6
14			4.4	3.0	1.4	180.0
15			5.3	6.8	−1.5	282.3
16			4.3	4.5	−0.2	188.5
17			4.4	6.3	−1.9	65.6
18			< 3.1			
19			< 3.0			
20			< 2.9			
21			3.3	1.6	1.7	255.5
22			4.6	3.7	0.9	10.5
23			2.5	1.0	1.5	116.1
24			1.9	2.0	−0.1	108.5
0	2	1	6.6	7.9	−1.3	240.4
1			4.5	4.9	−0.4	167.5
2			6.3	7.7	−1.4	110.8
3			14.3	9.1	5.2	342.5
4			20.1	23.5	−2.4	156.1
5			41.8	48.2	−6.4	250.7
6			40.2	33.7	6.5	342.5
7			15.2	15.9	−0.7	108.1
8			4.6	4.1	0.5	228.0
9			10.0	7.1	2.9	109.1
10			3.0	2.1	0.9	55.0
11			3.9	7.3	−3.4	40.5
12			4.5	4.9	−0.4	163.7
13			3.0	1.7	1.3	314.7
14			< 3.1			
15			4.7	4.9	−0.2	165.5
16			3.3	4.2	−0.9	182.3
17			5.3	5.9	−0.6	9.0
18			< 3.1			
19			< 3.0			
20			< 2.9			
21			< 2.6			
22			< 2.3			
23			< 2.0			
24			< 1.4			
0	2	2	11.4	14.7	−3.3	140.0
1			8.0	8.3	−0.3	28.0
2			9.0	5.5	3.5	192.1
3			8.2	1.8	6.4	351.1
4			17.8	15.8	2.0	190.7
5			13.4	9.5	3.9	338.8
6			11.0	10.4	0.6	5.2
7			4.0	3.2	0.8	45.7
8			6.3	5.5	0.8	48.1
9			2.9	4.5	−1.6	103.1
10			< 2.9			
11			4.9	3.6	1.3	216.8
12			< 3.0			
13			2.0	0.7	1.3	298.4
14			6.0	3.0	3.0	87.4
15			7.7	8.2	−0.5	176.1
16			6.5	8.0	−1.5	292.6
17			5.8	5.1	0.7	26.9
18			< 3.1			
19			< 2.9			
20			< 2.7			
21			< 2.5			
22			< 2.2			

h	k	l	Fo	Fc	ΔF	α°	h	k	l	Fo	Fc	ΔF	α°	h	k	l	Fo	Fc	ΔF	α°
23	2	2	< 1.1				15	2	5	< 2.9				$\bar{4}$	2	1	9.1	4.4	4.7	193.6
0	2	3	1.9	9.0	−7.1	67.2	16			< 2.7				$\bar{5}$			10.7	15.0	−4.3	5.8
1			2.4	3.9	−1.5	349.2	17			< 2.5				$\bar{6}$			5.7	3.4	2.3	100.9
2			8.6	8.9	−0.3	150.0	18			< 2.5				$\bar{7}$			10.0	8.8	1.2	176.5
3			< 2.3				19			4.1	3.1	1.0	205.6	$\bar{8}$			6.5	5.9	0.6	157.4
4			7.5	8.3	−0.8	15.0	20			4.7	5.4	−0.7	291.9	$\bar{9}$			3.9	3.2	0.7	79.9
5			6.2	5.8	0.4	137.3	0	2	6	< 3.2				$\bar{10}$			4.6	3.3	1.3	156.9
6			< 2.6				1			6.5	5.8	0.7	138.2	$\bar{11}$			5.1	4.6	0.5	20.9
7			3.5	2.6	0.9	21.7	2			< 3.2				$\bar{12}$			5.6	2.4	3.2	27.6
8			7.2	7.1	0.1	18.7	3			5.5	5.6	−0.1	338.4	$\bar{13}$			5.2	3.5	1.7	109.8
9			16.0	18.3	−2.3	289.6	4			4.1	4.9	−0.8	219.3	$\bar{14}$			3.4	5.0	−1.6	85.5
10			15.4	19.8	−4.4	189.7	5			< 3.2				$\bar{15}$			4.0	3.5	0.5	263.3
11			10.0	10.2	−0.2	75.7	6			< 3.2				$\bar{16}$			< 3.2			
12			5.3	4.9	0.4	333.2	7			< 3.2				$\bar{17}$			< 3.2			
13			3.2	4.0	−0.8	161.2	8			< 3.2				$\bar{18}$			< 3.1			
14			< 3.3				9			< 3.1				$\bar{19}$			3.3	2.2	1.1	272.3
15			2.5	1.4	1.1	184.4	10			< 3.1				$\bar{20}$			2.6	0.9	1.7	303.0
16			3.8	3.0	0.8	353.8	11			< 3.0				$\bar{21}$			5.7	4.3	1.4	211.6
17			< 3.2				12			< 3.0				$\bar{22}$			6.2	6.2	0.0	308.8
18			< 2.9				13			< 2.9				$\bar{23}$			5.5	5.9	−0.4	58.9
19			< 2.7				14			< 2.7				$\bar{24}$			4.1	4.7	−0.6	150.2
20			< 2.5				15			< 2.6				$\bar{1}$	2	2	16.9	17.9	−1.0	219.8
21			< 2.2				16			< 2.4				$\bar{2}$			14.2	16.3	−2.1	288.6
22			< 1.8				17			< 2.1				$\bar{3}$			6.6	7.4	−0.8	68.4
23			< 1.1				18			< 1.9				$\bar{4}$			14.0	10.0	4.0	337.1
0	2	4	6.3	6.3	0.0	277.7	0	2	7	< 3.1				$\bar{5}$			6.4	3.6	2.8	182.1
1			5.0	4.9	0.1	83.2	1			4.2	3.5	0.7	288.7	$\bar{6}$			3.5	4.2	−0.7	218.3
2			6.9	4.7	2.2	324.9	2			3.6	4.7	−1.1	309.2	$\bar{7}$			7.1	4.8	2.3	353.4
3			2.8	4.0	−1.2	104.3	3			10.8	13.0	−2.2	264.9	$\bar{8}$			2.3	2.0	0.3	154.0
4			< 2.8				4			6.5	5.1	1.4	337.5	$\bar{9}$			2.7	5.2	−2.5	235.1
5			< 2.8				5			3.9	3.0	0.9	291.2	$\bar{10}$			2.0	2.8	−0.8	313.1
6			< 2.9				6			3.0	2.9	0.1	231.2	$\bar{11}$			13.2	10.5	2.7	268.3
7			< 3.0				7			< 2.9				$\bar{12}$			8.2	9.2	−1.0	63.7
8			6.9	7.4	−0.5	327.1	8			< 2.8				$\bar{13}$			14.0	11.8	2.2	121.9
9			16.3	19.6	−3.3	266.4	9			< 2.7				$\bar{14}$			6.6	4.4	2.2	106.0
10			7.4	10.3	−2.9	111.6	10			< 2.6				$\bar{15}$			3.5	4.2	−0.7	25.6
11			7.0	8.6	−1.6	92.3	11			< 2.4				$\bar{16}$			< 3.2			
12			3.4	1.9	1.5	185.0	12			< 2.3				$\bar{17}$			< 3.1			
13			< 3.2				13			3.3	2.5	0.8	204.1	$\bar{18}$			< 3.1			
14			< 3.1				14			2.3	3.3	−1.0	118.0	$\bar{19}$			< 2.9			
15			< 3.1				15			2.1	2.7	−0.6	17.7	$\bar{20}$			< 2.8			
16			< 3.0				0	2	8	< 2.6				$\bar{21}$			< 2.5			
17			< 2.9				1			3.0	2.1	0.9	89.3	$\bar{22}$			5.1	6.1	−1.0	267.0
18			< 2.7				2			8.1	6.6	1.5	190.3	$\bar{23}$			< 1.8			
19			2.4	2.3	0.1	1.5	3			6.8	6.6	0.2	293.2	$\bar{24}$			1.6	3.3	−1.7	93.4
20			3.0	3.5	−0.5	266.7	4			5.8	4.3	1.5	35.3	$\bar{1}$	2	3	18.4	18.2	0.2	166.3
21			< 1.7				5			< 2.4				$\bar{2}$			7.9	7.8	0.1	292.1
0	2	5	< 3.0				6			< 2.3				$\bar{3}$			6.6	6.7	−0.1	46.8
1			< 3.0				7			< 2.2				$\bar{4}$			6.6	1.5	5.1	17.7
2			< 3.0				8			< 2.1				$\bar{5}$			3.4	4.8	−1.4	66.0
3			< 3.0				9			< 2.0				$\bar{6}$			4.7	3.8	0.9	300.2
4			< 3.1				10			< 1.8				$\bar{7}$			< 2.6			
5			< 3.1				11			< 1.5				$\bar{8}$			< 2.7			
6			< 3.1				0	2	9	< 1.6				$\bar{9}$			5.0	6.5	−0.5	351.6
7			< 3.2				1			< 1.6				$\bar{10}$			6.5	5.1	1.4	37.3
8			5.3	3.6	1.7	206.4	2			< 1.5				$\bar{11}$			15.6	17.9	−2.3	300.4
9			7.1	5.6	1.5	334.8	3			< 1.4				$\bar{12}$			13.5	15.0	−1.5	197.1
10			3.4	4.2	−0.8	63.9	4			< 1.3				$\bar{13}$			12.8	16.1	−3.3	90.5
11			7.8	6.3	1.5	156.4	5			< 0.9				$\bar{14}$			3.0	4.2	−1.2	317.6
12			3.0	4.0	−1.0	57.3	$\bar{1}$	2	1	7.5	12.3	−4.8	86.2	$\bar{15}$			3.6	2.3	1.3	90.6
13			< 3.1				$\bar{2}$			4.9	2.7	2.2	329.5	$\bar{16}$			< 3.1			
14			< 3.0				$\bar{3}$			4.4	3.4	1.0	56.9	$\bar{17}$			< 3.1			

h	k	l	F_o	F_c	ΔF	α°
$\bar{18}$	2	3	< 3.0			
$\bar{19}$			< 2.8			
$\bar{20}$			< 2.6			
$\bar{21}$			< 2.3			
$\bar{22}$			< 1.9			
$\bar{23}$			2.2	2.9	0.7	184.1
$\bar{1}$	2	4	12.6	12.7	0.1	222.6
$\bar{2}$			10.0	13.3	3.3	116.9
$\bar{3}$			5.9	7.3	1.4	21.3
$\bar{4}$			3.9	2.1	1.8	250.4
$\bar{5}$			3.8	3.1	0.7	99.0
$\bar{6}$			< 2.8			
$\bar{7}$			< 2.9			
$\bar{8}$			< 3.0			
$\bar{9}$			< 3.1			
$\bar{10}$			5.2	5.5	0.3	100.7
$\bar{11}$			6.0	2.9	3.1	351.9
$\bar{12}$			7.6	7.8	0.2	217.2
$\bar{13}$			5.6	5.6	0.0	155.1
$\bar{14}$			5.5	4.5	1.0	5.6
$\bar{15}$			2.8	0.9	1.9	9.6
$\bar{16}$			3.3	1.3	2.0	37.2
$\bar{17}$			3.8	3.6	0.2	201.5
$\bar{18}$			3.3	3.3	0.0	295.4
$\bar{19}$			4.5	3.0	1.5	350.3
$\bar{20}$			< 2.2			
$\bar{21}$			< 1.8			
$\bar{22}$			< 1.3			
$\bar{1}$	2	5	2.3	4.0	1.7	257.7
$\bar{2}$			5.6	5.2	0.4	187.7
$\bar{3}$			2.8	1.3	1.5	56.1
$\bar{4}$			4.8	3.0	1.8	209.5
$\bar{5}$			6.5	5.2	1.3	358.6
$\bar{6}$			7.1	6.4	0.7	172.4
$\bar{7}$			10.5	11.4	0.9	247.7
$\bar{8}$			13.7	14.2	0.5	346.9
$\bar{9}$			6.2	5.7	0.5	93.8
$\bar{10}$			5.7	3.9	1.8	116.6
$\bar{11}$			4.5	3.2	1.3	138.9
$\bar{12}$			< 3.1			
$\bar{13}$			2.9	2.3	0.6	349.8
$\bar{14}$			3.6	2.5	1.1	199.0
$\bar{15}$			3.0	2.6	0.4	152.9
$\bar{16}$			4.6	3.7	0.9	347.7
$\bar{17}$			3.1	2.5	0.6	136.0
$\bar{18}$			3.0	3.0	0.0	211.7
$\bar{19}$			3.9	4.0	0.1	343.8
$\bar{20}$			2.5	2.3	0.2	76.1
$\bar{1}$	2	6	< 3.2			
$\bar{2}$			< 3.2			
$\bar{3}$			< 3.2			
$\bar{4}$			3.4	4.0	0.6	126.8
$\bar{5}$			< 3.2			
$\bar{6}$			4.2	5.3	1.1	72.2
$\bar{7}$			6.0	8.9	2.9	246.5
$\bar{8}$			10.9	13.1	2.1	289.3
$\bar{9}$			7.1	7.2	0.1	75.9
$\bar{10}$			< 3.1			
$\bar{11}$			< 3.0			
$\bar{12}$			< 2.9			
$\bar{13}$			< 2.8			
$\bar{14}$			< 2.7			
$\bar{15}$	2	6	< 2.5			
$\bar{16}$			< 2.3			
$\bar{17}$			< 2.0			
$\bar{18}$			< 1.6			
$\bar{19}$			< 0.8			
$\bar{1}$	2	7	< 3.1			
$\bar{2}$			< 3.1			
$\bar{3}$			< 3.1			
$\bar{4}$			< 3.0			
$\bar{5}$			3.7	1.2	2.5	286.2
$\bar{6}$			5.8	2.6	3.2	159.6
$\bar{7}$			3.4	5.0	1.6	11.9
$\bar{8}$			4.3	4.7	0.4	264.7
$\bar{9}$			< 2.8			
$\bar{10}$			< 2.7			
$\bar{11}$			< 2.5			
$\bar{12}$			< 2.4			
$\bar{13}$			< 2.2			
$\bar{14}$			< 2.0			
$\bar{15}$			< 1.7			
$\bar{16}$			< 1.2			
$\bar{1}$	2	8	< 2.6			
$\bar{2}$			< 2.6			
$\bar{3}$			< 2.5			
$\bar{4}$			< 2.5			
$\bar{5}$			< 2.5			
$\bar{6}$			< 2.4			
$\bar{7}$			< 2.3			
$\bar{8}$			< 2.2			
$\bar{9}$			< 2.1			
$\bar{10}$			< 1.9			
$\bar{11}$			< 1.7			
$\bar{12}$			< 1.4			
$\bar{1}$	2	9	2.2	0.3	1.9	47.4
$\bar{2}$			3.1	2.4	0.7	49.9
$\bar{3}$			2.6	3.5	0.9	169.0
$\bar{4}$			< 1.3			
$\bar{5}$			< 1.2			
$\bar{6}$			< 0.7			
1	3	0	4.2	1.7	2.5	169.7
2			8.1	10.5	2.4	142.5
3			7.6	15.7	8.1	15.8
4			2.3	2.8	0.5	157.8
5			4.3	2.5	1.8	177.2
6			4.5	2.2	2.3	185.9
7			5.3	2.7	2.6	194.2
8			3.2	2.9	0.3	335.7
9			2.3	3.0	0.7	194.8
10			2.2	1.3	0.9	159.4
11			2.8	1.9	0.9	321.4
12			3.5	4.4	0.9	49.5
13			4.2	5.6	1.4	298.7
14			2.4	4.5	2.1	216.6
15			< 1.8			
16			< 1.7			
17			< 1.7			
18			< 1.6			
19			< 1.5			
20			< 1.3			
21			< 1.1			
22			< 0.4			
0	3	1	[illegible]	[illegible]	0.5	118.7
1	3	1	2.6	6.0	3.4	208
2			< 1.0			
3			5.5	3.9	1.6	113.5
4			5.5	3.7	1.8	30.6
5			2.1	2.3	0.2	151.1
6			2.8	3.4	0.6	353.7
7			8.4	11.4	3.0	155.4
8			12.1	16.0	3.9	216.1
9			14.5	14.7	0.2	333.2
10			4.7	3.3	1.4	93.1
11			< 1.7			
12			3.2	2.3	0.9	36.7
13			2.1	3.5	1.4	264.3
14			2.0	1.7	0.3	61.6
15			< 1.8			
16			2.9	1.4	1.5	118.0
17			< 1.7			
18			< 1.6			
19			< 1.4			
20			< 1.2			
21			< 1.0			
0	3	2	3.3	0.8	2.5	317.2
1			1.8	0.9	0.9	256.8
2			1.6	2.4	0.8	178.2
3			1.7	3.0	1.3	197.8
4			4.2	2.6	1.6	97.7
5			6.3	4.6	1.7	202.9
6			9.0	9.5	0.5	87.6
7			9.7	8.2	1.5	134.9
8			19.6	20.9	1.3	274.2
9			5.8	5.6	0.2	9.2
10			5.8	2.8	3.0	69.1
11			2.1	2.0	0.1	7.0
12			2.0	1.8	0.2	73.2
13			< 1.8			
14			< 1.8			
15			< 1.7			
16			< 1.7			
17			< 1.6			
18			3.2	3.5	0.3	149.8
19			2.9	3.4	0.5	352.9
20			2.7	2.6	0.1	12.1
21			< 0.7			
0	3	3	2.6	2.6	0.0	174.0
1			2.1	3.2	1.1	166.3
2			2.3	3.2	0.9	25.8
3			4.2	1.8	2.4	318.1
4			3.0	2.8	0.2	68.9
5			4.5	6.6	2.1	178.2
6			12.3	13.1	0.8	98.4
7			10.1	17.8	7.7	303.5
8			6.5	10.3	3.8	303.5
9			3.6	3.2	0.4	100.1
10			3.4	4.2	0.8	314.9
11			2.0	2.0	0.0	135.0
12			1.9	0.7	1.2	19.3
13			< 1.8			
14			< 1.7			
15			< 1.7			
16			< 1.6			
17			3.6	3.4	0.2	106.8
18			< 1.3			

h	k	l	F_o	F_c	ΔF	α°
19	3	3	3.3	3.4	−0.1	270.1
0	3	4	3.4	5.7	−2.3	350.7
1			5.4	6.6	−1.2	96.2
2			6.3	4.4	1.9	197.4
3			3.9	2.0	1.9	253.1
4						
5			3.0	2.0	1.0	171.5
6			3.6	4.3	−0.7	39.9
7			4.0	4.1	−0.1	318.0
8			< 1.8			
9			3.8	2.6	1.2	240.6
10			3.5	4.3	−0.8	188.2
11			< 1.8			
12			< 1.7			
13			< 1.7			
14			< 1.6			
15			< 1.5			
16			< 1.4			
17			< 1.2			
18			2.1	3.2	−1.1	335.4
19			< 0.5			
0	3	5	2.7	2.7	0.0	67.0
1			4.9	6.7	−1.8	122.0
2			4.5	5.8	−1.3	244.2
3			< 1.8			
4			< 1.8			
5			< 1.8			
6			< 1.8			
7			< 1.8			
8			< 1.8			
9			< 1.7			
10			< 1.7			
11			2.6	2.7	−0.1	215.3
12			4.2	4.2	0.0	316.7
13			3.4	3.1	0.3	34.4
14			2.8	3.0	−0.2	131.0
15			< 1.2			
16			< 1.1			
17			< 0.7			
0	3	6	3.7	5.2	−1.5	140.1
1			2.8	4.6	−1.8	14.7
2			< 1.7			
3			< 1.7			
4			< 1.7			
5			< 1.7			
6			< 1.7			
7			< 1.6			
8			< 1.6			
9			< 1.5			
10			< 1.5			
11			3.9	3.8	0.1	286.5
12			< 1.3			
13			2.8	2.4	0.4	101.8
14			< 0.9			
0	3	7	< 1.5			
1			< 1.5			
2			< 1.5			
3			< 1.5			
4			< 1.4			
5			< 1.4			
6			3.0	3.2	−0.2	222.3
7			2.9	1.6	1.3	327.4

h	k	l	F_o	F_c	ΔF	α°
8	3	7	3.2	0.9	2.3	119.8
9			< 1.1			
10			< 1.0			
11			< 0.6			
0	3	8	< 1.0			
1			< 0.9			
2			< 0.9			
3			< 0.9			
4			< 0.8			
5			< 0.5			
$\bar{1}$	3	1	7.0	4.7	2.3	110.7
$\bar{2}$			7.0	11.1	−4.1	328.3
$\bar{3}$			11.8	10.8	1.0	263.6
$\bar{4}$			9.9	7.5	2.2	99.4
$\bar{5}$			4.0	2.7	1.3	83.1
$\bar{6}$			3.3	2.4	0.9	154.2
$\bar{7}$			1.8	2.6	−0.8	35.5
$\bar{8}$			1.9	2.6	−0.7	185.1
$\bar{9}$			2.5	1.3	1.2	318.9
$\bar{10}$			3.3	2.0	1.3	294.5
$\bar{11}$			< 1.7			
$\bar{12}$			3.2	2.4	0.8	238.4
$\bar{13}$			2.9	1.3	1.6	140.2
$\bar{14}$			5.7	5.6	0.1	115.6
$\bar{15}$			5.5	3.4	2.1	252.5
$\bar{16}$			< 1.7			
$\bar{17}$			< 1.7			
$\bar{18}$			< 1.6			
$\bar{19}$			< 1.4			
$\bar{20}$			< 1.3			
$\bar{21}$			< 1.0			
$\bar{1}$	3	2	4.2	5.1	−0.9	340.1
$\bar{2}$			4.9	8.2	−3.3	166.6
$\bar{3}$			10.3	11.0	−0.7	272.1
$\bar{4}$			8.3	11.0	−2.7	11.4
$\bar{5}$			7.2	6.5	0.7	104.7
$\bar{6}$			2.7	3.0	−0.3	213.0
$\bar{7}$			3.0	2.3	0.7	130.7
$\bar{8}$			3.3	0.9	2.4	244.9
$\bar{9}$			< 1.7			
$\bar{10}$			3.7	4.6	−0.9	158.8
$\bar{11}$			5.7	4.1	1.6	31.1
$\bar{12}$			4.1	5.1	−1.0	358.2
$\bar{13}$			< 1.8			
$\bar{14}$			< 1.8			
$\bar{15}$			4.6	6.7	−2.1	182.2
$\bar{16}$			3.1	3.0	0.1	309.4
$\bar{17}$			< 1.6			
$\bar{18}$			< 1.5			
$\bar{19}$			< 1.4			
$\bar{20}$			< 1.2			
$\bar{21}$			< 0.9			
$\bar{1}$	3	3	2.4	3.0	−0.6	324.6
$\bar{2}$			4.1	1.2	2.9	225.3
$\bar{3}$			< 1.6			
$\bar{4}$			5.4	3.0	1.4	283.2
$\bar{5}$			3.4	2.5	0.9	59.4
$\bar{6}$			2.6	3.6	−1.0	208.0
$\bar{7}$			3.4	2.3	1.1	17.2
$\bar{8}$			7.0	7.7	−0.7	264.2
$\bar{9}$			10.4	11.9	−1.5	164.5
$\bar{10}$			4.0	6.9	−2.9	69.1

h	k	l	F_o	F_c	ΔF	α°
$\bar{11}$	3	3	2.7	4.3	−1.6	[illegible]
$\bar{12}$			< 1.8			
$\bar{13}$			< 1.8			
$\bar{14}$			< 1.8			
$\bar{15}$			< 1.7			
$\bar{16}$			< 1.7			
$\bar{17}$			< 1.6			
$\bar{18}$			< 1.5			
$\bar{19}$			< 1.2			
$\bar{20}$			< 0.9			
$\bar{1}$	3	4	3.3	1.6	1.7	139.2
$\bar{2}$			2.1	1.5	0.6	209.1
$\bar{3}$			2.8	5.5	−2.7	358.2
$\bar{4}$			< 1.7			
$\bar{5}$			< 1.8			
$\bar{6}$			3.5	3.3	0.2	296.2
$\bar{7}$			4.0	3.0	1.0	95.0
$\bar{8}$			6.3	6.9	−0.6	290.8
$\bar{9}$			7.0	7.3	−0.3	219.4
$\bar{10}$			12.6	14.2	−1.6	104.3
$\bar{11}$			3.0	2.8	0.2	358.6
$\bar{12}$			5.5	3.9	1.6	213.1
$\bar{13}$			< 1.7			
$\bar{14}$			< 1.7			
$\bar{15}$			< 1.6			
$\bar{16}$			< 1.5			
$\bar{17}$			< 1.3			
$\bar{18}$			< 1.1			
$\bar{19}$			< 0.9			
$\bar{1}$	3	5	3.6	2.6	1.0	264.8
$\bar{2}$			< 1.8			
$\bar{3}$			< 1.8			
$\bar{4}$			< 1.8			
$\bar{5}$			< 1.8			
$\bar{6}$			< 1.8			
$\bar{7}$			3.2	2.1	1.1	6.7
$\bar{8}$			3.7	2.5	1.2	128.0
$\bar{9}$			6.5	6.4	0.1	308.1
$\bar{10}$			6.9	8.8	−1.9	48.9
$\bar{11}$			7.4	8.8	−1.4	165.7
$\bar{12}$			5.5	3.8	1.7	238.2
$\bar{13}$			2.0	1.7	0.3	339.4
$\bar{14}$			< 1.4			
$\bar{15}$			< 1.3			
$\bar{16}$			< 1.2			
$\bar{17}$			< 0.9			
$\bar{1}$	3	6	2.8	3.2	−0.4	202.4
$\bar{2}$			< 1.7			
$\bar{3}$			< 1.7			
$\bar{4}$			< 1.7			
$\bar{5}$			< 1.7			
$\bar{6}$			< 1.7			
$\bar{7}$			< 1.6			
$\bar{8}$			< 1.6			
$\bar{9}$			< 1.6			
$\bar{10}$			< 1.5			
$\bar{11}$			< 1.4			
$\bar{12}$			< 1.3			
$\bar{13}$			< 1.2			
$\bar{14}$			< 1.1			
$\bar{15}$			< 0.8			
$\bar{1}$	3	7	< 1.5			

h	k	l	F_o	F_c	ΔF	α°
$\bar{2}$	3	7	< 1.5			
$\bar{3}$			< 1.5			
$\bar{4}$			3.5	4.6	−1.1	322.3
$\bar{5}$			3.5	3.5	0.0	239.1
$\bar{6}$			2.5	2.8	−0.3	155.2
$\bar{7}$			< 1.3			
$\bar{8}$	3	7	< 1.3			
$\bar{9}$			< 1.2			
$\bar{10}$			< 1.1			
$\bar{11}$			< 0.9			
$\bar{12}$			< 0.4			
$\bar{1}$	3	8	< 1.0			
$\bar{2}$	3	8	< 0.9			
$\bar{3}$			< 0.9			
$\bar{4}$			< 0.9			
$\bar{5}$			< 0.7			
$\bar{6}$			< 0.3			

h	k	l	F_o	h	k	l	F_o
$\bar{4}$	$\bar{8}$	4	5.1	$\bar{7}$	$\bar{3}$	4	14.6
	$\bar{9}$		9.1		$\bar{4}$		5.3
	$\overline{10}$		5.1		$\bar{5}$		7.1
	$\overline{11}$		10.4		$\bar{6}$		7.3
	$\overline{12}$		1.6		$\bar{7}$		7.2
	$\overline{13}$		4.8		$\bar{8}$		4.3
	$\overline{14}$		4.8		$\bar{9}$		< 1.2
	$\overline{15}$		< 0.7		$\overline{10}$		6.1
	$\overline{16}$		< 0.7		$\overline{11}$		4.6
$\bar{5}$	$\bar{1}$	4	2.4		$\overline{12}$		4.0
	$\bar{2}$		2.4		$\overline{13}$		< 0.6
	$\bar{3}$		< 1.0	$\bar{8}$	$\bar{1}$	4	8.4
	$\bar{4}$		11.4		$\bar{2}$		3.3
	$\bar{5}$		11.2		$\bar{3}$		9.1
	$\bar{6}$		4.8		$\bar{4}$		3.6
	$\bar{7}$		1.9		$\bar{5}$		1.9
	$\bar{8}$		2.4		$\bar{6}$		2.7
	$\bar{9}$		1.7		$\bar{7}$		1.2
	$\overline{10}$		8.2		$\bar{8}$		1.4
	$\overline{11}$		< 1.1		$\bar{9}$		1.2
	$\overline{12}$		3.0		$\overline{10}$		1.1
	$\overline{13}$		4.7		$\overline{11}$		0.7
	$\overline{14}$		1.6		$\overline{12}$		< 0.2
	$\overline{15}$		2.1	$\bar{9}$	$\bar{1}$	4	< 1.2
$\bar{6}$	$\bar{1}$	4	7.1		$\bar{2}$		8.6
	$\bar{2}$		2.9		$\bar{3}$		< 1.1
	$\bar{3}$		1.7		$\bar{4}$		2.7
	$\bar{4}$		4.7		$\bar{5}$		5.6
	$\bar{5}$		5.5		$\bar{6}$		< 1.0
	$\bar{6}$		7.8		$\bar{7}$		2.6
	$\bar{7}$		13.0		$\bar{8}$		4.1
	$\bar{8}$		4.3		$\bar{9}$		3.2
	$\bar{9}$		< 1.2	$\overline{10}$	$\bar{1}$	4	2.6
	$\overline{10}$		6.3		$\bar{2}$		< 0.9
	$\overline{11}$		2.6		$\bar{3}$		4.3
	$\overline{12}$		3.6		$\bar{4}$		< 0.7
	$\overline{13}$		4.8		$\bar{5}$		1.1
	$\overline{14}$		1.2		$\bar{6}$		3.0
$\bar{7}$	$\bar{1}$	4	6.0		$\bar{7}$		1.2
	$\bar{2}$		6.3				

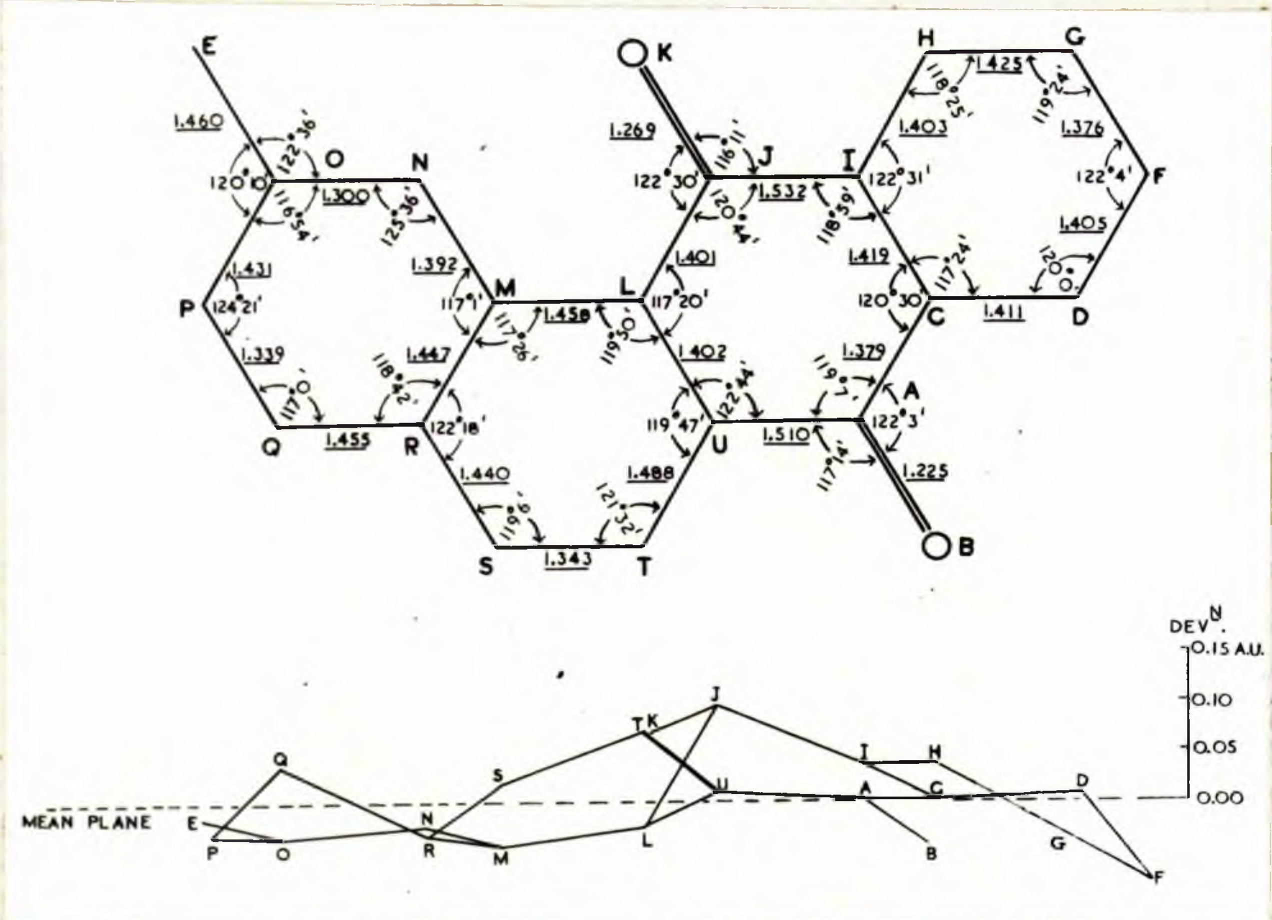


Fig. 4.7. The bond lengths and bond angles of 2'-methyl 1:2-benzanthraquinone. The deviations of the atoms from the mean molecular plane are also indicated.

(d) Discussion of the Structure.

To simplify the subsequent calculations, the monoclinic co-ordinates (x, y, z) given in Table 4,7 were converted to rectangular co-ordinates (x', y, z') by the following transformation

$$x' = x - z\cos\beta^{*}$$

$$y = y$$

$$z' = z\sin\beta^{*}$$

From these co-ordinates the values of the bond lengths and bond angles found in this investigation were calculated and the values obtained are listed in Table 4,11(a) and (b) and illustrated in Fig. 4,7. The mean bond lengths and bond angles of the aromatic rings DFGHIC, TULMRS and EMNOPQ are (1.407 A.U., 119°58'), (1.430 A.U., 120°1') and (1.394 A.U., 119°57') respectively. The overall mean bond length for the three aromatic rings is 1.408 A.U. and the mean bond angle is 119°59'.

The principle of least squares was used to calculate the mean molecular plane, which was found to be

$$-0.4569x' - 0.8582y - 0.2338z' + 3.1592 = 0$$

The deviations of the individual atoms from the above plane are given along with the calculated bond lengths in Table 4,11(b). The maximum deviations occur in the atoms K,F,J and T, in which the deviations are 0.069 A.U., 0.082 A.U., 0.095 A.U. and 0.068 A.U. respectively. The mean deviation from the plane is 0.036 A.U. and root mean square deviation is 0.044 A.U.

TABLE 4.11.

(a) The calculated bond lengths of 2'-methyl 1:2-benzanthraquinone and their standard deviations (σ).

(Values in A.U.)

BOND	BOND LENGTH	σ	BOND	BOND LENGTH	σ
AB	1.225	0.020	ML	1.458	0.025
AC	1.379	0.025	MN	1.392	0.023
AU	1.510	0.025	MR	1.447	0.026
CD	1.411	0.026	ON	1.300	0.030
CI	1.419	0.023	OE	1.460	0.028
FD	1.405	0.027	OP	1.431	0.029
FG	1.376	0.025	QP	1.339	0.028
HG	1.425	0.027	QR	1.455	0.028
HI	1.403	0.026	SR	1.440	0.025
JI	1.532	0.026	ST	1.343	0.029
JK	1.269	0.020	TU	1.488	0.025
JL	1.401	0.025	UL	1.402	0.023

Mean aromatic bond length = 1.408 A.U.

TABLE 4.11.

(b) The calculated bond angles of 2'-methyl 1:2-benzanthraquinone and the deviations of the atoms from the mean molecular plane.

BOND ANGLE	ANGLE	BOND ANGLE	ANGLE	ATOM	DEVIATION (A.U.)
UAB	117°14'	ULM	119°50'	B	-0.043
BAC	122°3'	LMR	117°26'	K	0.069
UAC	119°7'	RMN	117°1'	A	0.001
ACI	120°30'	MNO	125°36'	C	-0.001
ICD	117°24'	NOE	122°36'	D	0.005
CDF	120°0'	NOP	116°54'	E	-0.016
DFG	122°4'	EOP	120°10'	F	-0.082
FGH	119°23'	OPQ	124°28'	G	-0.040
GHI	118°25'	PQR	117°0'	H	0.037
HIC	122°31'	QRM	118°42'	I	0.035
CIJ	118°59'	MRS	122°18'	J	0.095
IJK	116°11'	RST	119°6'	K	-0.025
KJL	122°30'	STU	121°32'	M	-0.044
IJL	120°44'	TUL	119°47'	N	-0.024
JLU	117°20'	LUA	122°44'	O	-0.037
				P	-0.033
				Q	0.040
				R	-0.033
				S	0.019
				T	0.068
				U	0.009

Mean deviation from the plane = 0.036 A.U.

Root mean square deviation = 0.044 A.U.

TABLE 4.12.

The standard deviations (σ) of the atomic co-ordinates used to calculate the structure factors of the last cycle of three-dimensional least squares refinement.

ATOM	σ_x (A.U.)	σ_y (A.U.)	σ_z (A.U.)
B	0.0117	0.0205	0.0116
K	0.0115	0.0194	0.0116
A	0.0158	0.0224	0.0161
C	0.0157	0.0241	0.0161
D	0.0177	0.0231	0.0167
E	0.0201	0.0337	0.0208
F	0.0182	0.0289	0.0188
G	0.0168	0.0289	0.0173
H	0.0165	0.0274	0.0162
I	0.0158	0.0250	0.0163
J	0.0162	0.0241	0.0165
L	0.0157	0.0232	0.0152
M	0.0159	0.0232	0.0166
N	0.0169	0.0274	0.0172
O	0.0185	0.0289	0.0182
P	0.0190	0.0289	0.0197
Q	0.0186	0.0289	0.0186
R	0.0165	0.0250	0.0176
S	0.0180	0.0250	0.0183
T	0.0173	0.0274	0.0168
U	0.0159	0.0232	0.0166
MEAN	0.0166	0.0256	0.0168

The standard deviations of the atomic co-ordinates were calculated from equations of the type,

$$\left[\sigma\left(\frac{x_i}{a}\right)\right]^2 = \sum \omega \Delta F^2 \Big/ (n-s) \sum \omega \left(\frac{\delta F_c}{\delta \frac{x_i}{a}}\right)$$

where n is the number of independent structure factors and s is the number of parameters which are refined. The estimated standard deviations of the co-ordinates used to calculate the last cycle of least squares refinement are shown in Table 4,12 and these will be used to define the upper limits of the standard deviations of the final set of atomic co-ordinates and the bond lengths calculated from these co-ordinates.

As in the structure of 5-methyl 1:2-benzanthraquinone the standard deviations of the atomic co-ordinates are not equal and hence the standard deviation of the bond length between two symmetrically independent atoms was calculated using the method outlined in Chapter III section (e) and the values are given along with calculated bond lengths in Table 4,11(a).

The statistical levels of significance suggested by Cruickshank (Chapter III section (e)) were used in the investigation of the significance of the bond lengths and the deviations of the atoms from the mean molecular plane.

The C = O bond lengths AB and JK are not significantly different from the values found for 5-methyl 1:2-benzanthraquinone. The most surprising feature of the structure is that the bond lengths AC and LJ are significantly shorter than the expected C – C single bond length of 1.51 A.U. They are also significantly shorter than the other two single C – C bond lengths AU and IJ. A theoretical reason for this is very difficult to find and it may be that as in the case of 5-methyl

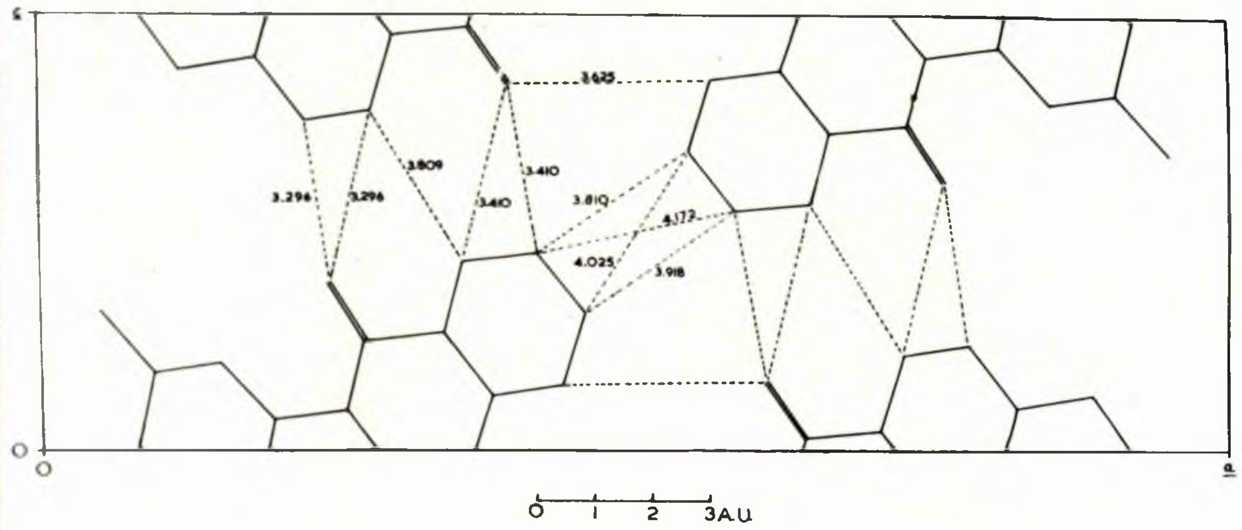


Fig. 4.8. The projection of the contents of the unit cell down the **b** - axis showing the intermolecular contacts of < 4.20 A.U.

1:2-benzanthraquinone, the bond lengths AC and LJ may change quite considerably on further refinement, in which case there must be some doubt about the estimated standard deviations of the atomic co-ordinates.

An investigation of the significance of the deviations of the atoms from the mean molecular plane showed that the deviations of the atoms K,J,F and T are all significant, whereas the deviations of the atoms B and M are only possibly significant.

The packing arrangement of the molecules in the unit cell is illustrated in Fig. 4,8 and the intermolecular contacts of < 4.20 A.U., are drawn. The values of the short C - O and C - C intermolecular contacts are very similar to the values found in the structure of 5-methyl 1:2-benzanthraquinone.

(e) Comparison of the Structures of 5-Methyl 1:2-Benzanthraquinone and 2'-Methyl 1:2-Benzanthraquinone.

The most marked difference between the two structures is in the bond lengths AC and LJ, those of the 2'-methyl derivitive being significantly shorter than the corresponding bond lengths in 5-methyl 1:2-benzanthraquinone.

In the structure of 5-methyl 1:2-benzanthraquinone there are some marked deviations from the mean molecular plane, especially in the atoms N and O and there is a distinct possibility that this is caused by the overcrowding in the structure of the oxygen atom at K and the carbon atom and its associated hydrogen atom at N. Some work has been carried out in recent years on overcrowded structures (Herbstein and Schmidt, 1954)

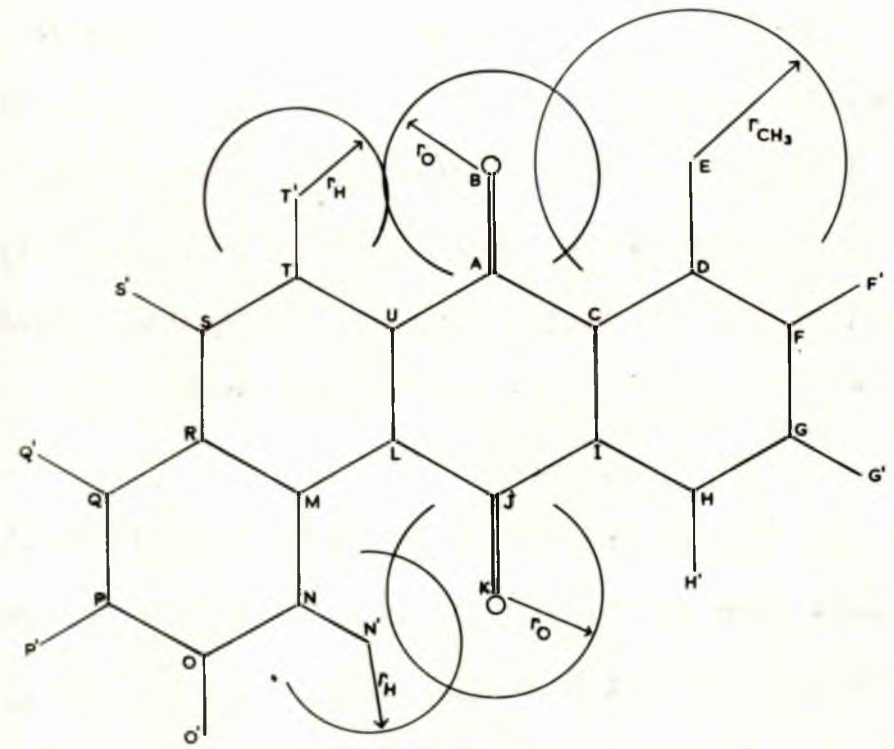


Fig. 4.9. The molecule of 5-methyl 1:2-benzanthraquinone. The circles represent the Van der Waals spheres for the appropriate atoms.

and in a paper to the Kekule Symposium, Coulson (Coulson, 1958) has discussed the possibility of overcrowding in structure of the type 5-methyl 1:2-benzanthracene. If the theoretical model of 5-methyl 1:2-benzanthraquinone in Fig. 4,9 is considered (all the bond angles are assumed to be 120.0° and the bond lengths are as given in Fig. 4,1) and circles representing the Van der Waals spheres are drawn for the methyl group, the oxygen atoms B and K and the hydrogen atom N', it is obvious that there will be repulsive forces acting between the oxygen atom K and the hydrogen atom N' and between the methyl group at E and the oxygen atom B. The calculated distance between the atoms K and N on the above model is 2.54 A.U., whereas the observed distance is 2.76 A.U. with a standard deviation of 0.023 A.U. In the same way the calculated distance between the atoms N' and K is 1.76 A.U. and the value using the estimated co-ordinates of the hydrogen atom N' would be 2.05 A.U. It is therefore possible that in order to ease the overcrowding, the atoms N', N and K are displaced from the mean molecular plane, the atoms O and P also being displaced but to a lesser extent. The actual difference in the deviations of the atoms N and K (0.31 A.U.) does not account for the whole of the difference between the calculated and the observed values of the distance NK. The bond length LM is significantly longer and the bond length MN possibly significantly longer than the mean aromatic bond length and it seems likely that both the deviations from the mean plane and the adjustments of the bond length in the particular region of the molecule take part in helping to relieve the overcrowding.

The theoretical distance between the carbon atom at E and the oxygen atom at B is 2.54 A.U., whereas the observed value is 2.70 A.U. with a standard deviation of 0.023 A.U. The signs of the deviations of the atoms from the mean molecular plane are the same and the difference between them is only 0.034 A.U. The angle between the bond lengths AB and DE is about 5° and it might be that the overcrowding has been eased by an adjustment of the bond angles in the region BACDE, of the molecule the atoms B and E being pushed apart.

In view of the possibility of overcrowding of the atoms N' and K in 2'-methyl 1:2-benzanthraquinone, it is very surprising that the bond length LJ is significantly shorter than the normal value for a C – C single bond length. The actual distance between the atoms K and N is 2.77 A.U. with a standard deviation of 0.025 A.U. compared with the calculated value of 2.54 A.U. Although the deviations of the atoms N and K have different signs, the actual difference is only 0.09 A.U. The angle between the two bonds JK and MN is however 11°, which is fairly large and it seems very likely that there is an adjustment of the bond angles in the region of the molecule KJLMN such that the atoms K and N are pushed apart.

Since the preceeding arguments are not conclusive because the accuracy of the structures is limited, it will be very interesting to see whether the same effects are observed when the structures have been determined as accurately as possible.

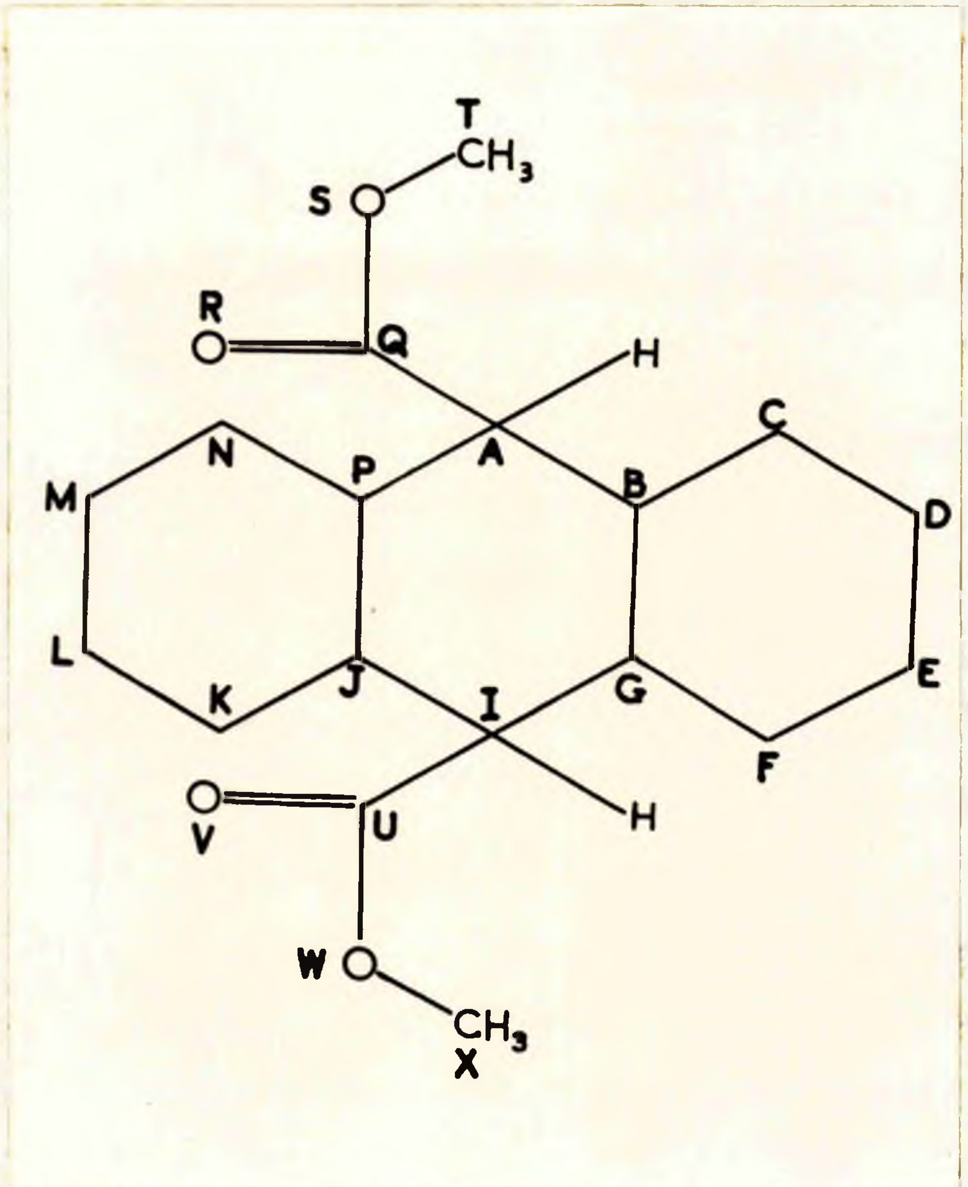


Fig. 5.1. The molecule of cis-9:10-dimethoxy-carbonyl 9:10-dihydro-anthracene, showing the lettering of the atoms adopted in the investigation.

CHAPTER V.

THE CRYSTAL STRUCTURE OF THE CIS-ISOMER OF 9,10-DIMETHOXY-CARBONYL 9,10-DIHYDROANTHRACENE ($C_{18}H_{16}O_4$).

(a) Previous Work.

A sketch of the molecule is shown in Fig. 5,1. The indexing as indicated in this diagram will be followed throughout this chapter.

It has been shown (Ferrier and Iball, 1955) that the 9,10-dihydroanthracene molecule is not planar but is bent about the line joining the carbon atoms 9 and 10 to produce a folded structure (Fig. 5,2). Beckett and Mulley (Beckett and Mulley, 1955) have stated that with this type of molecule there are two geometrically distinct carbon-hydrogen bonds in the meso or 9,10 carbon positions. Two of these bonds are orientated in a direction opposite to which the molecule is folded and are almost perpendicular to the line joining the carbon atoms 9 and 10. They designated these bonds 'perp' bonds. The bonds of the other pair are directed away from the centre of the molecule and are designated 'lin' - abbreviation for linear - bonds (Fig. 5,2). They have also stated that if two similar groups in which mutually repulsive forces are operative e.g. two methoxy-carbonyl groups are substituted in the 9,10 positions, the cis-configuration would tend to favour the 'lin-lin'

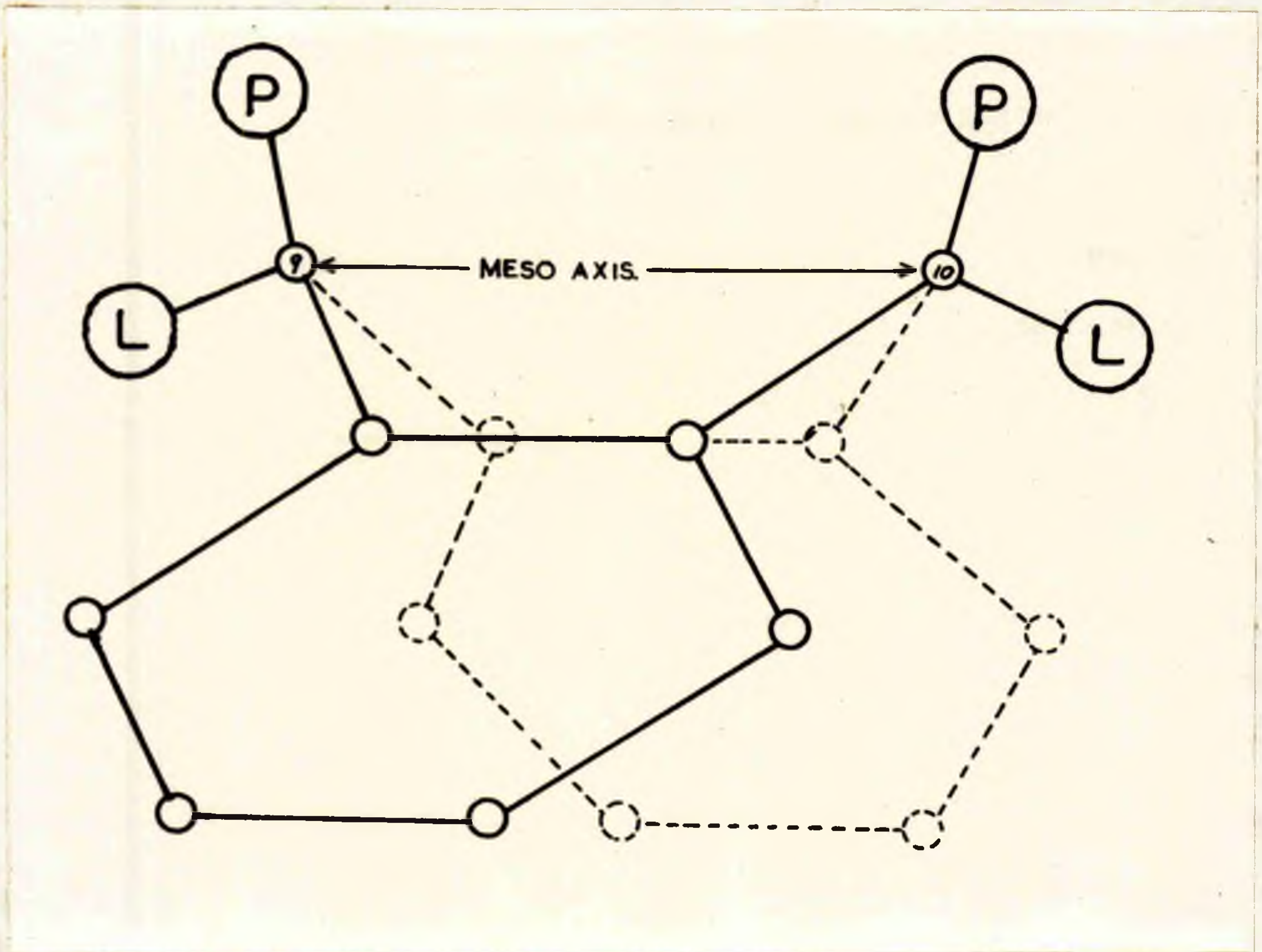


Fig. 5.2. The folded molecule of 9:10-dihydroanthracene.

P - "perp" positions.

L - "lin" positions.

position in which there would be greater group separation than in the 'perp-perp' form. However an approximate vectorial summation of moments indicates that the ratio of dipole moments of the trans- to the cis-isomer of 9,10-dimethoxy-carbonyl 9,10-dihydroanthracene would be 100 if the two methoxy-carbonyl groups are both 'lin' in the cis-compound and approximately 0.7 if they are both 'perp'. The dipole moments have been measured (Bergmann and Weizmann, 1938) and the ratio is approximately 0.65. There is therefore considerable evidence that, at least in solution, the methoxy-carbonyl groups are in the 'perp-perp' positions.

The sample of the cis-isomer of 9,10 dimethoxy-carbonyl 9,10-dihydroanthracene was supplied by Dr. A.H. Beckett of the School of Pharmacy, Chelsea Polytechnic. The compound crystallises in large clear equidimensional crystals with many prominent faces. The space-group and unit cell dimensions have been determined (Mackay, 1958) and are as follows:-

$\underline{a}$	= 8.379 A.U.	α =	$99°40'$
$\underline{b}$	= 13.201 A.U.	β =	$116°37'$
$\underline{c}$	= 7.554 A.U.	γ =	$87°50'$
d_{100}	= 7.486 A.U.	α^* =	$80°15'$
d_{010}	= 13.005 A.U.	β^* =	$63°21'$
d_{001}	= 6.656 A.U.	γ^* =	$87°35'$

Number of molecules in the unit cell	=	2
Volume of the unit cell	=	367.9 A.U.^{3}
Observed density	=	1.338 g./cc.^{3}
Calculated density	=	1.338 g./cc.^{3}

There are no systematic absences and the space-group is either P1 or $P\bar{1}$.

(b) Preliminary Investigation.

The crystals were examined and the results quoted by Mackay for the space-group and unit cell dimensions were confirmed.

Equi-inclination Weissenberg photographs were taken about the a, b and c - axes of rotation using molybdenum radiation and a large rhombohedral-shaped crystal of side approximately 1.0 mm. Three films of different sensitivities were used for each exposure - Ilford "Industrial G.", Ilford "Industrial B.", Ilford "Industrial C.". The interfilm absorption ratios were found by internal correlation of the visually estimated intensities. These ratios were found to be,

G:B = 3.5:1 B:C = 3.8:1

Using a small equidimensional crystal and copper Kα radiation, equi-inclination Weissenberg photographs were taken as follows:-

zero layer and upper layer lines one to four of the a - axis,
zero layer and upper layer lines one to four of the c - axis,
zero layer and upper layer lines one to eight of the b - axis.

Time did not permit the estimation of the intensities of the upper layer lines of the a and b - axes. The reflected intensities on the other photographs were estimated visually and in addition the stronger intensities of the (hk0) and (0kl) zones were measured on the Geiger counter spectrometer. The zero layer line intensities were corrected for the usual Lorentz and polarisation factors and the intensities of upper layers of the c - axis were corrected using Cochran's chart.

An attempt was made to put the relative values of the corrected intensities of the (hk0) zone on the absolute scale using Wilson's method. The scatter of points on the resulting graph was such that no conclusion could be made regarding the scale factor. A possible explanation of the failure of Wilson's method is that there may be overlapping of the atoms in the methoxy-carbonyl groups in this projection.

By comparison with the parent compound 9:10-dihydroanthracene, it was decided to use an overall temperature factor of B = 3.0 A.U.^{2}. The relative intensities were scaled such that the highest unitary structure factor in the (hk0) zone had a value of 0.6. In the initial stages an oxygen atom was assumed to have a scattering power $^4/_3$ that of a carbon atom and the scattering curve used was that of Berghuis et. al., for carbon suitably adjusted for temperature effect.

The N(Z) test (Howells, Phillips and Rogers, 1950) was applied to the data in the three main zones in order to test for a centre of symmetry. The reflections were divided into equal groups of sin θ

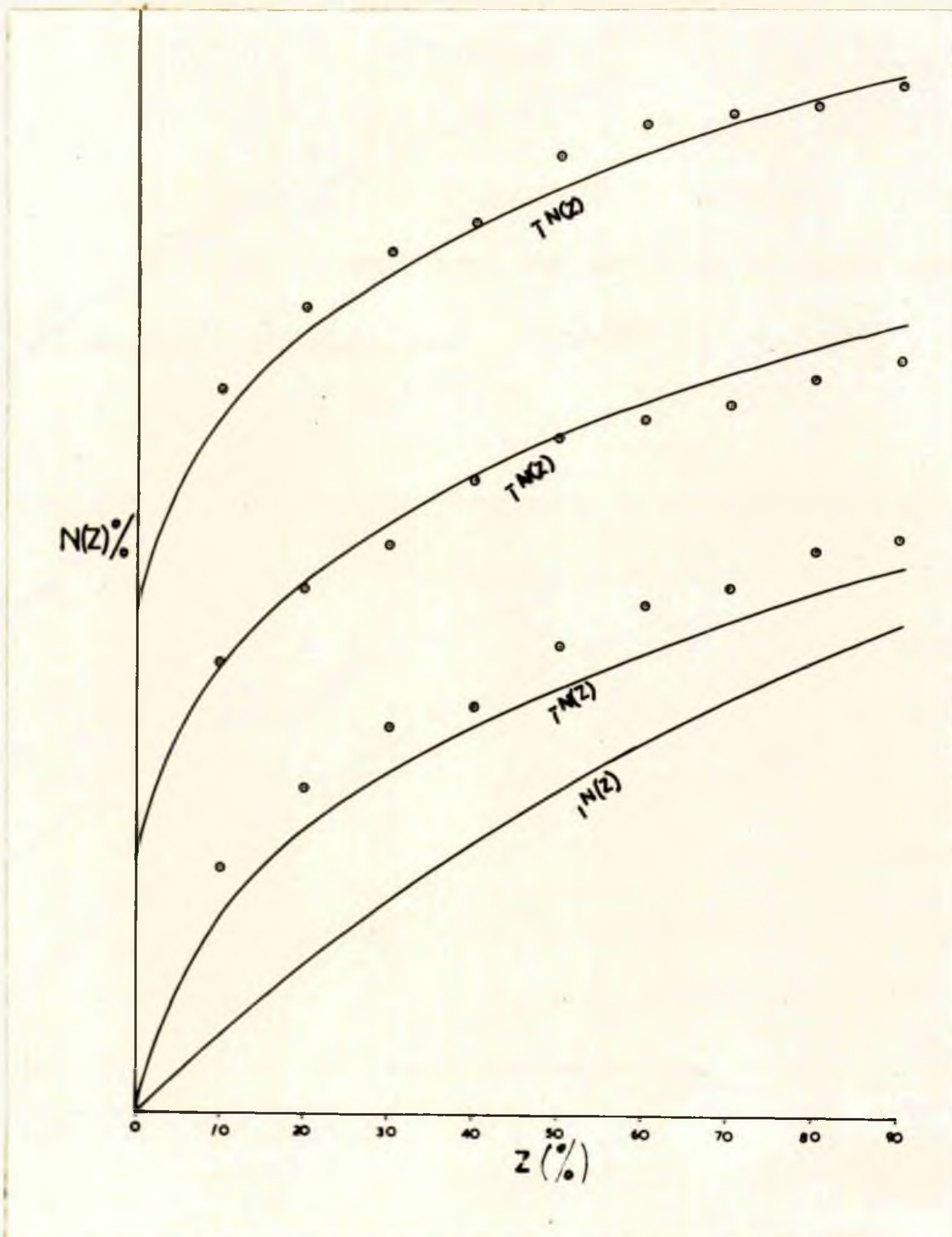


Fig. 5.3. Graphs showing the results of the N(Z) test on the three principal zones of cis-9:10-dimethoxy-carbonyl 9:10-dihydroanthracene.

and the average value of $\langle I \rangle$ was calculated for each group. Each intensity was then expressed as a fraction $Z = {}^{I}/\langle I \rangle$ of the average intensity for the corresponding group. The fractions $N(Z)$ of reflections whose intensities are less than or equal to Z are,

$$_{1}N(Z) = 1 - \exp.(-Z) \qquad \text{———} \qquad (1)$$

$$_{\bar{1}}N(Z) = \text{erf.}(\tfrac{1}{2}Z)^{\frac{1}{2}} \qquad \text{———} \qquad (2)$$

for the non centrosymmetric and centrosymmetric cases respectively. The mean $N(Z)$ for $Z = 10, 20, \ldots\ldots\ldots, 100\%$ was plotted and compared with the theoretical curves (1) and (2).

The results are shown in Fig. 5,3 and clearly indicate that each zone is in fact centrosymmetric and hence the crystal was assigned to the space-group $P\bar{1}$.

(c) Determination of the Approximate Structure.

(i) Direct Method.

The direct method of Harker-Kasper relationships (Chap.IV, sect.(b,1)) was applied to the data collected from the (hk0) zone in which there was a possibility of resolution. As before, the relation

$$(U_H \pm U_{H'})^2 \leqslant (1 \pm U_{H+H'})\ (1 \pm U_{H-H'})$$

was the only inequality which proved useful. Several sign relationships were found and are shown in Table 5,1. No signs were determined uniquely and the method failed to solve the structure. There is a degree of doubt about some of the relationships because of the uncertainty in the scale factor.

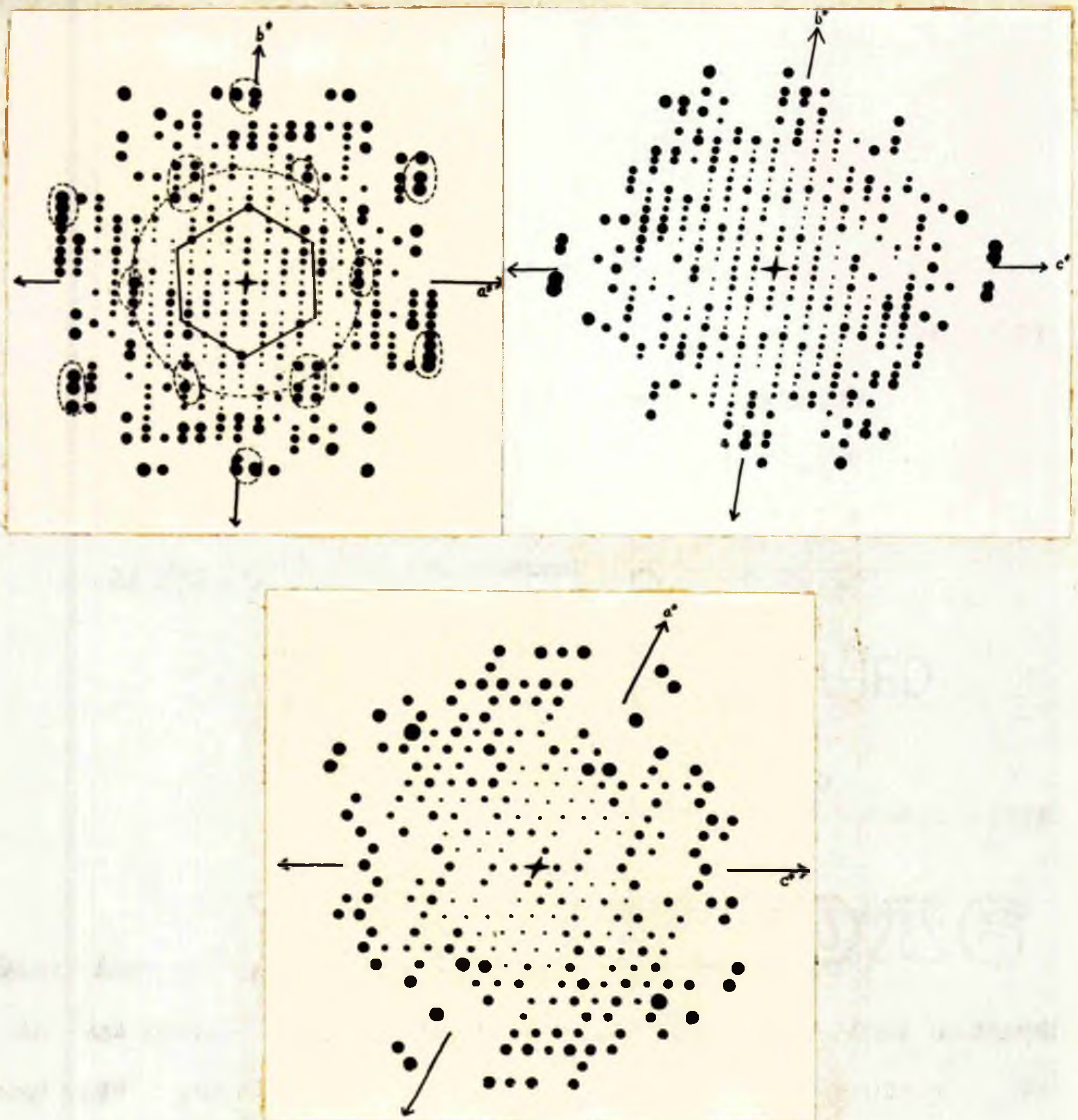


Fig. 5.4. (a) The weighted reciprocal lattice of the (hk0) zone.

(b) The weighted reciprocal lattice of the (0kl) zone.

(c) The weighted reciprocal lattice of the (h0l) zone.

TABLE 5.1.

Harker-Kasper sign relationships for the structure factors of the (hk0) zone.

S(9 5 0)	=	-S($\bar{3}$ 5 0)		
S(9 10 0)	=	S(6 0 0) S(3 10 0)		
S($\bar{7}$ 14 0)	=	-S(5 14 0)		
S(5 18 0)	=	S($\bar{7}$ 18 0)	=	S(6 0 0) S($\bar{1}$ 18 0)
S(3 8 0)	=	-S($\bar{9}$ 8 0)		
S($\overline{10}$ 8 0)	=	S(6 0 0) S($\bar{4}$ 8 0)		

where S means 'the sign of'.

(ii) Trial and Error Methods.

Theoretical considerations indicate that the most probable structure is that in which the anthracene nucleus is folded and the methoxy-carbonyl groups are in the 'perp-perp' positions. This however does not exclude the possibility that in the crystal form the methoxy-carbonyl groups are 'lin-lin'. It is also possible that the anthracene nucleus may have a 'strained' planar structure, and in the initial stages all three possibilities were examined .

The weighted reciprocal lattices, of the three axial zones, weighted in accordance with the unitary structure factors, were drawn out and are shown in Fig. 5,4(a), (b) and (c). The weighted reciprocal

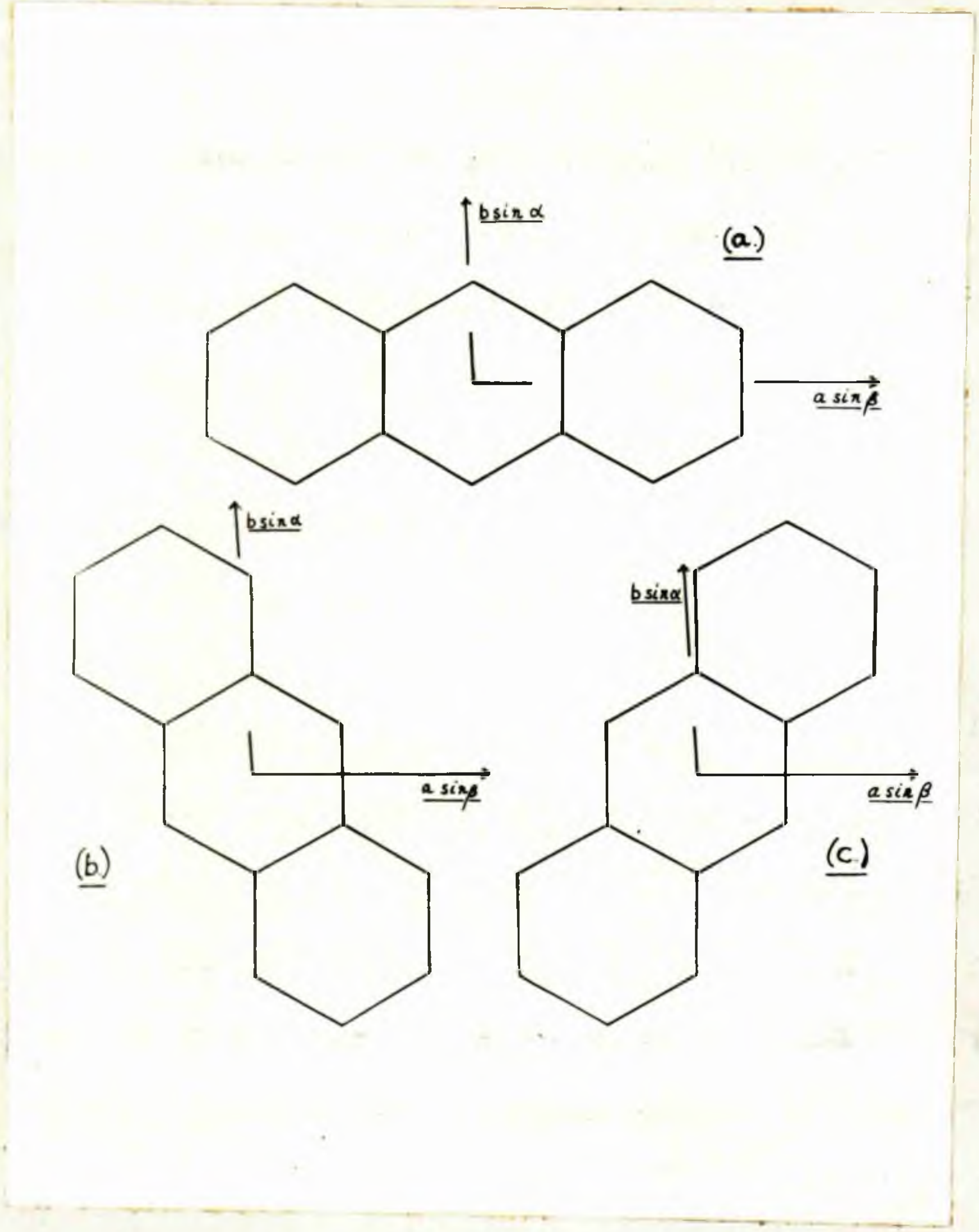


Fig. 5.5. (a), (b) and (c) show the three ways in which the anthracene part of the molecule can be built up from the basic benzene ring derived from the weighted reciprocal lattice of the (h0l) zone.

lattice of the (hk0) zone exhibited well defined benzene ring groups and it was decided to concentrate on this projection in the initial stages. The centres of gravity of the benzene ring groups were estimated and the 'mean' benzene ring was calculated. There are three possible ways in which the anthracene nucleus can be built up from the basic unit and these are shown in Fig. 5,5(a), (b) and (c).

The Weissenberg photograph of the (hk0) zone taken with molybdenum radiation showed distinct diffuse regions of scattering around the benzene ring groups and these diffus regions extended well beyond the limit of the normal copper radiation. The shapes of these diffuse regions are shown by dotted lines in Fig. 5,4(a). The elongation of these regions in the direction $\underline{b}^*$ seemed to indicate that the length of the anthracene nucleus should lie along the direction $\underline{a\sin\beta}$. This orientation indicated by (a) in Fig. 5,5 was investigated. Attempts were made to fit a folded structure with the methoxy-carbonyl groups in the 'perp-perp' position and in the 'lin-lin' position without success. A further attempt to fit a planar structure was also unsuccessful.

The axial structure factors are such that $F_o(010)$ has a very low value. This indicates that if the methoxyl-carbonyl groups are to be placed reasonably symmetrically with respect to the anthracene nucleus, the molecular centre cannot lie very far from the position $y/\underline{b\sin\alpha} = 0.25$ in the direction $\underline{b\sin\alpha}$. The value of $F_o(600)$ is

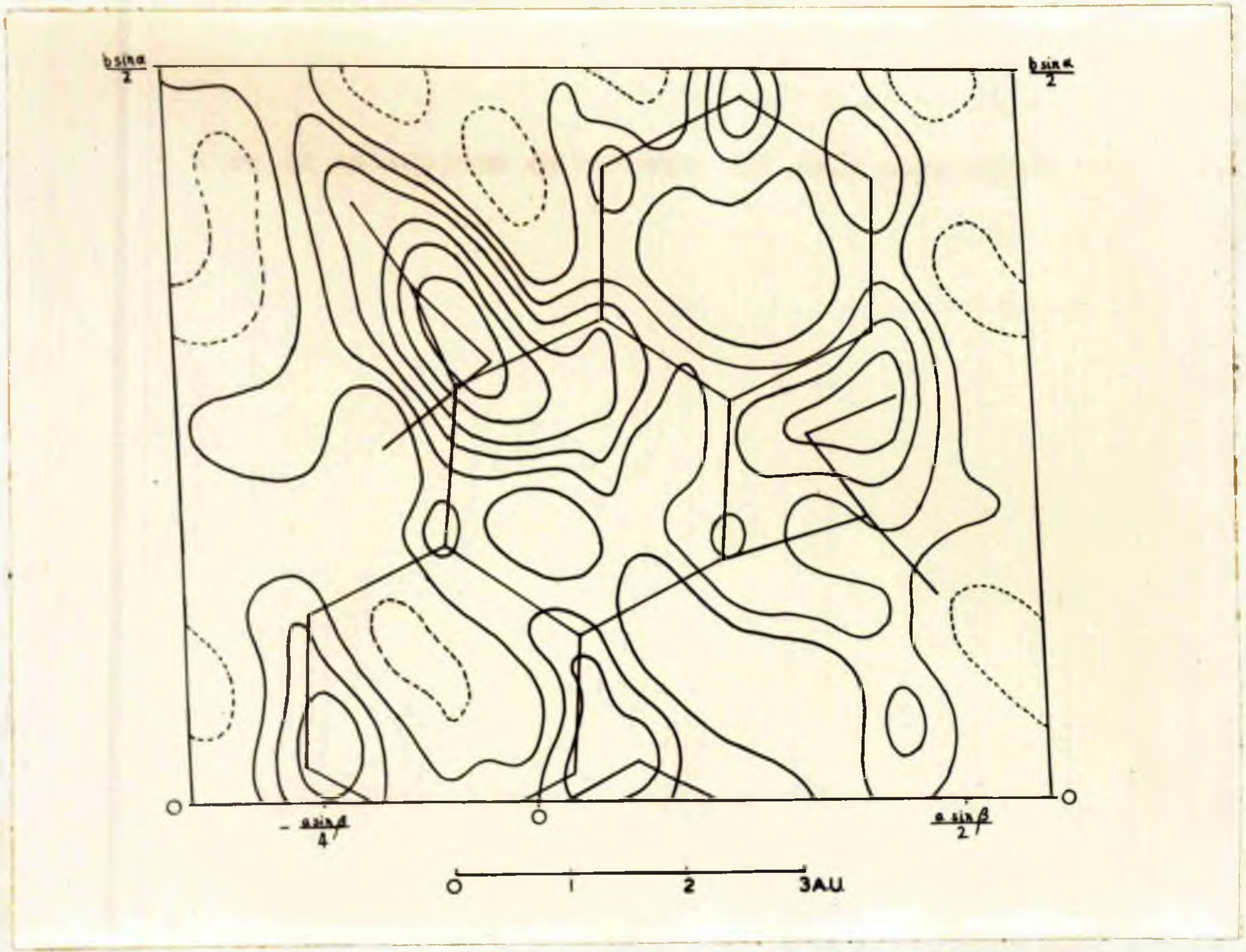


Fig. 5.6. The initial Fourier map of the (hk0) projection. The 1 e./A.U.^{2} contour is dotted and the other contours are drawn at arbitrary intervals.

relatively high and the $\sin\theta$ value of the reflection corresponds to a spacing of 1.22 A.U., which indicates that the molecular centre must lie close to one of, $x/\underline{a\sin\beta}$ = 0.000, 0.083, 0.167, 0.250, 0.333, 0.417. $F_o(100)$ is fairly strong, which would mean that the position $x/\underline{a\sin\beta}$ = 0.250 is unlikely. Attempts were now made to fit folded and planar structures with the anthracene nucleus as in Fig. 5,5(b), but without success.

The third possible orientation of the anthracene nucleus was now investigated and the only reasonable fit between the observed and calculated structure factors of the reflections with low indices was obtained with a structure having the anthracene nucleus planar and tilted through an angle of approximately 25° about the line joining the carbon atoms 9 and 10. The molecular centre was placed at (0.083 $\underline{a\sin\beta}$, 0.220 $\underline{b\sin\alpha}$). The co-ordinates of the molecule in this position are shown in Table 5,2. The phases derived from a structure factor calculation were used to compute a Fourier synthesis and the resulting map of electron density is shown in Fig. 5,6. The map seemed quite encouraging although it was clear that the atoms T and V were not in the correct position. Several attempts were made to refine the structure without success.

Having failed to obtain a solution in the (hk0) projection, it was decided to investigate the other two axial zones. However mainly due to the uncertainty about the orientation of the molecule, no useful

TABLE 5.2.

Atomic x and y co-ordinates.

ATOM.	$x/a\sin\gamma$	$y/b\sin\alpha$.
A	-0.067	0.277
B	0.103	0.327
C	0.113	0.425
D	0.270	0.480
E	0.423	0.425
F	0.420	0.318
G	0.263	0.272
I	0.237	0.177
J	0.057	0.112
K	0.060	0.022
L	-0.120	-0.025
M	-0.260	0.022
N	-0.260	0.120
P	-0.097	0.177
Q	-0.117	0.352
T	-0.193	0.242
U	0.403	0.192
X	0.440	0.275
R	-0.187	0.410
S	-0.030	0.300
V	0.473	0.138
W	0.333	0.250

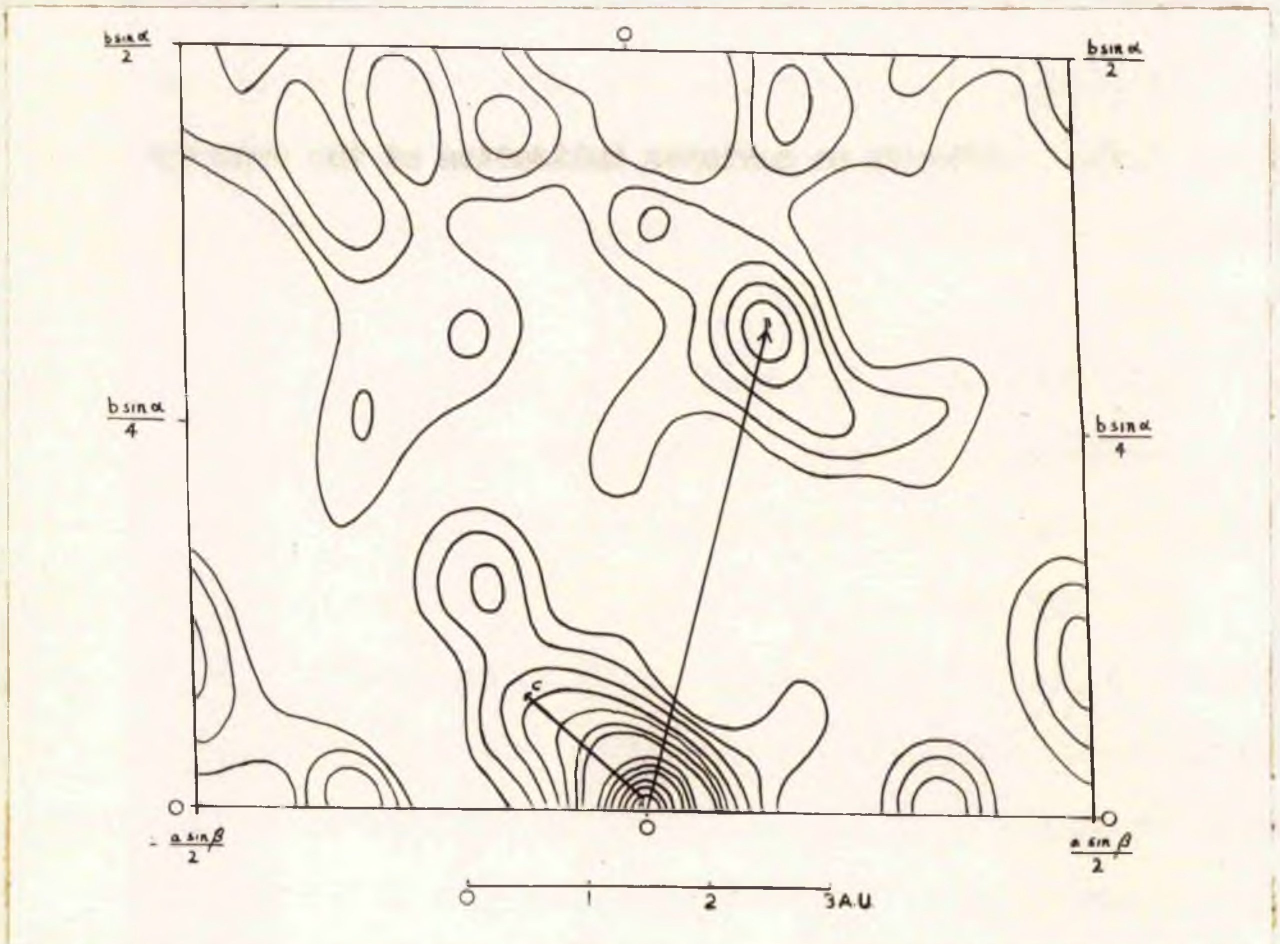


Fig. 5.7. The Patterson map of the (hk0) zone. The $|F(000)|^2$ term has been omitted and the contours are drawn at arbitrary intervals.

information was derived.

In view of the great difficulty in determining the orientation of the anthracene nucleus, it was decided to compute the two-dimensional (hk0) projection of the Patterson Function (Chap.IV, sect. (b,ii)). The Patterson synthesis was computed and the contour map was drawn (Fig. 5,7). Although no definite indication of the orientation of the molecule was obtained from the Patterson map, there were two interesting features.

(1) The vector distance 1.4 A.U. is reinforced in the direction AC. This would appear to indicate that several of the bonds of methoxy-carbonyl groups lie in this direction.

(2) The strongest peak in the vector field is at B. The vector length AB is equal to 4.3 A.U., and it is difficult to see how this can be the sum of intramolecular vectors. The most likely explanation is that the vector is the sum of the vectors between corresponding atoms in the anthracene parts of the molecules related through the centre of symmetry at the origin of the projection. This would mean that the molecular centre is at approximately (0.075 <u>a sin β</u>, 0.160 <u>b sin α</u>). Attempts were made to fit a molecule with its centre placed at this point, but the value of the F(010) structure factor always calculated much too high.

The values of the observed structure factors are given in Table 5,3.

(d) <u>Conclusion</u>.

The attempt to find an approximate structure indicates that, even when the orientation of the anthracene nucleus is derived, the methoxy-carbonyl groups must be placed with reasonable accuracy if a fit is to be obtained between the observed and calculated structure factors. It is hoped that a three-dimensional Patterson synthesis will be computed at a later date and that the interpretation will lead to a solution of the structure.

Appendix. The Development of Colour in the Crystals of cis- 9:10-Dimethoxy-Carbonyl 9:10-Dihydroanthracene on Irradiation with X-rays.

After prolonged irradiation with x-rays, it was observed that the colourless crystals of cis- 9:10-dimethoxy-carbonyl 9:10-dihydroanthracene exhibited dichroism, the crystals showing a distinct pink colour in the direction of the optic axis perpendicular to the (100) plane. No significant difference could be detected between structure factors measured with a new crystal and with the same crystal after it had changed colour.

The exact reason for the effect is not yet known, but it is probably due to the formation of free radicals and the crystals are being studied by Dr. D. Bijl of the Physics Department of St. Andrews University, using the technique of electron paramagnetic resonance. The results of this work were not available at the time of writing.

TABLE 5,3

THE OBSERVED STRUCTURE FACTORS OF CIS-9:10-DIMETHOXY-CARBONYL 9:10-DIHYDROANTHRACENE.

h	k	l	Fo	h	k	l	Fo	h	k	l	Fo	h	k	l	Fo	h	k	l	Fo	h	k	l	Fo
0	1	0	6.2	0	12	2	2.2	0	14	5	< 2.5	0	$\bar{14}$	1	< 0.6	0	$\bar{10}$	4	9.4	0	$\bar{6}$	7	0.5
	2		31.0		13		5.1		15		3.0		$\bar{15}$		3.6		$\bar{11}$		5.6		$\bar{7}$		1.4
	3		21.1		14		2.0	0	0	6	1.0		$\bar{16}$		1.3		$\bar{12}$		4.4		$\bar{8}$		4.8
	4		23.2		15		0.9		1		2.7		$\bar{17}$		2.4		$\bar{13}$		4.2		$\bar{9}$		4.5
	5		1.5		16		< 0.3		2		4.4		$\bar{18}$		2.4		$\bar{14}$		< 0.5		$\bar{10}$		3.1
	6		< 0.4	0	0	3	< 0.6		3		< 0.6		$\bar{19}$		< 2.6		$\bar{15}$		2.2		$\bar{11}$		2.5
	7		16.1		1		3.3		4		< 0.6		$\bar{20}$		2.5		$\bar{16}$		1.4		$\bar{12}$		2.9
	8		8.9		2		1.6		5		< 0.6	0	$\bar{1}$	2	18.0		$\bar{17}$		2.8		$\bar{13}$		< 0.3
	9		3.5		3		2.4		6		< 0.6		$\bar{2}$		6.9	0	$\bar{1}$	5	9.6		$\bar{14}$		< 2.5
	10		3.6		4		14.9		7		< 0.5		$\bar{3}$		25.7		$\bar{2}$		< 0.5		$\bar{15}$		< 2.6
	11		1.1		5		4.6		8		3.0		$\bar{4}$		17.1		$\bar{3}$		4.7		$\bar{16}$		< 2.6
	12		2.2		6		13.4		9		1.9		$\bar{5}$		10.2		$\bar{4}$		8.2		$\bar{17}$		3.9
	13		8.1		7		< 0.5		10		< 0.6		$\bar{6}$		12.6		$\bar{5}$		4.5	0	$\bar{1}$	8	< 0.6
	14		4.0		8		7.0	0	0	7	4.0		$\bar{7}$		< 0.5		$\bar{6}$		7.3		$\bar{2}$		2.8
	15		3.4		9		3.7		1		0.9		$\bar{8}$		14.1		$\bar{7}$		11.7		$\bar{3}$		0.8
	16		6.4		10		2.9		2		2.2		$\bar{9}$		3.7		$\bar{8}$		2.2		$\bar{4}$		1.0
	17		3.1		11		< 0.6		3		1.6		$\bar{10}$		2.8		$\bar{9}$		1.1		$\bar{5}$		5.8
	18		4.0		12		1.0		4		2.7		$\bar{11}$		4.2		$\bar{10}$		0.8		$\bar{6}$		2.0
	19		2.6		13		1.8		5		3.0		$\bar{12}$		2.5		$\bar{11}$		3.6		$\bar{7}$		1.1
0	0	1	22.1		14		0.9		6		1.2		$\bar{13}$		8.4		$\bar{12}$		< 0.6		$\bar{8}$		1.9
	1		2.9		15		< 0.4		7		< 0.4		$\bar{14}$		0.9		$\bar{13}$		5.5		$\bar{9}$		2.3
	2		11.4	0	0	4	14.4		8		3.8		$\bar{15}$		< 0.5		$\bar{14}$		2.3		$\bar{10}$		2.7
	3		42.9		1		17.9	0	0	8	1.3		$\bar{16}$		1.1		$\bar{15}$		0.6	0	$\bar{1}$	9	3.0
	4		25.6		2		1.5		1		< 0.5		$\bar{17}$		< 0.4		$\bar{16}$		3.9		$\bar{2}$		< 2.4
	5		2.4		3		1.3		2		3.2	0	$\bar{1}$	3	8.9		$\bar{17}$		< 2.5		$\bar{3}$		< 2.4
	6		4.7		4		2.4		3		1.7		$\bar{2}$		3.7		$\bar{18}$		2.6		$\bar{4}$		< 2.4
	7		2.4		5		4.7		4		< 0.4		$\bar{3}$		11.5		$\bar{19}$		< 2.7		$\bar{5}$		4.5
	8		11.3		6		< 0.5		5		2.4		$\bar{4}$		2.4		$\bar{20}$		3.2	0	$\bar{1}$	11	2.7
	9		2.8		7		5.6		6		< 2.8		$\bar{5}$		0.8	0	$\bar{1}$	6	< 0.6		$\bar{2}$		3.1
	10		4.1		8		5.7	0	0	9	< 2.5		$\bar{6}$		2.7		$\bar{2}$		1.9		$\bar{3}$		2.4
	11		1.7		9		7.5		1		< 2.5		$\bar{7}$		12.9		$\bar{3}$		3.8	1	0	0	25.0
	12		3.2		10		0.6		2		< 2.5		$\bar{8}$		4.1		$\bar{4}$		13.3	2			6.0
	13		1.4		11		< 0.5		3		< 2.5		$\bar{9}$		6.7		$\bar{5}$		5.7	3			3.1
	14		2.2		12		4.9		4		< 2.6		$\bar{10}$		3.6		$\bar{6}$		2.6	4			2.6
	15		2.0		13		1.1		5		4.0		$\bar{11}$		8.5		$\bar{7}$		4.1	5			2.9
	16		2.6		14		< 0.3	0	1	11	3.6		$\bar{12}$		1.0		$\bar{8}$		5.5	6			21.1
	17		< 2.4	0	0	5	< 0.8		2		3.2		$\bar{13}$		5.6		$\bar{9}$		1.9	7			4.1
	18		2.6		1		1.4	0	$\bar{1}$	1	28.4		$\bar{14}$		4.0		$\bar{10}$		1.3	8			1.1
0	0	2	21.1		2		< 0.5		$\bar{2}$		20.5		$\bar{15}$		< 0.5		$\bar{11}$		3.1	9			< 0.6
	1		26.0		3		6.6		$\bar{3}$		27.0		$\bar{16}$		1.2		$\bar{12}$		4.3	10			< 2.1
	2		25.8		4		< 0.6		$\bar{4}$		1.3		$\bar{17}$		< 0.3		$\bar{13}$		1.5	11			1.1
	3		3.0		5		9.9		$\bar{5}$		24.8	0	$\bar{1}$	4	5.0		$\bar{14}$		2.3	1	0	1	2.7
	4		10.3		6		< 0.6		$\bar{6}$		8.6		$\bar{2}$		15.2		$\bar{15}$		< 2.4	2			1.0
	5		5.2		7		6.0		$\bar{7}$		22.9		$\bar{3}$		2.1		$\bar{16}$		2.3	3			6.3
	6		5.0		8		2.5		$\bar{8}$		3.2		$\bar{4}$		11.5		$\bar{17}$		3.6	4			2.7
	7		16.2		9		< 0.5		$\bar{9}$		4.7		$\bar{5}$		8.6	0	$\bar{1}$	7	3.5	5			8.1
	8		< 0.5		10		< 0.5		$\bar{10}$		5.4		$\bar{6}$		18.1		$\bar{2}$		3.9	6			18.9
	9		5.2		11		< 0.5		$\bar{11}$		2.0		$\bar{7}$		9.2		$\bar{3}$		6.6	7			2.6
	10		< 0.6		12		1.7		$\bar{12}$		5.0		$\bar{8}$		3.1		$\bar{4}$		8.1	8			< 0.6
	11		1.0		13		2.8		$\bar{13}$		2.3		$\bar{9}$		3.4		$\bar{5}$		7.9	9			1.4

h	k	l	F_o	h	k	l	F_o	h	k	l	F_o	h	k	l	F_o	h	k	l	F_o	h	k	l	F_o
10	0	1	< 2.2	$\bar{8}$	0	2	1.1	$\bar{9}$	0	7	2.9	2	11	0	2.8	6	8	0	< 2.0	$\bar{2}$	12	0	4.2
11			< 2.2	$\bar{9}$			1.7	$\bar{10}$			< 0.6		12		3.1		9		3.3		13		3.5
12			4.6	$\bar{10}$			1.2	$\bar{11}$			2.9		13		1.7		10		< 0.5		14		1.9
1	0	2	13.2	$\bar{1}$	0	3	4.2	$\bar{12}$			1.8		14		5.6		11		1.2		15		< 2.0
2			1.4	$\bar{2}$			1.7	$\bar{13}$			2.2		15		4.1		12		< 0.3		16		1.4
3			5.0	$\bar{3}$			2.5	$\bar{1}$	0	8	3.8		16		< 0.3		13		4.4		17		< 2.4
4			9.7	$\bar{4}$			9.1	$\bar{2}$			< 0.8	3	1	0	6.8		14		< 2.4		18		3.1
5			9.3	$\bar{5}$			5.7	$\bar{3}$			2.6		2		16.7		15		2.9	$\bar{3}$	1	0	17.8
6			< 0.8	$\bar{6}$			3.4	$\bar{4}$			2.3		3		24.2	7	1	0	4.5		2		4.4
7			< 0.8	$\bar{7}$			0.9	$\bar{5}$			1.8		4		12.8		2		4.4		3		1.9
8			< 0.6	$\bar{8}$			3.3	$\bar{6}$			3.2		5		30.7		3		4.8		4		20.6
9			< 2.2	$\bar{9}$			2.8	$\bar{7}$			2.0		6		1.1		4		< 0.6		5		11.6
10			< 2.4	$\bar{10}$			3.0	$\bar{8}$			1.6		7		8.6		5		3.3		6		5.5
11			2.5	$\bar{11}$			3.6	$\bar{9}$			< 0.4		8		14.2		6		1.8		7		2.8
1	0	3	0.9	$\bar{12}$			< 2.2	$\bar{10}$			2.5		9		2.2		7		1.7		8		18.6
2			5.3	$\bar{13}$			2.5	$\bar{11}$			2.0		10		13.4		8		< 0.5		9		1.7
3			2.4	$\bar{1}$	0	4	2.2	$\bar{1}$	0	9	< 0.8		11		3.8		9		< 0.4		10		11.6
4			< 0.8	$\bar{2}$			9.5	$\bar{2}$			2.7		12		3.5		10		1.8		11		10.8
5			4.1	$\bar{3}$			2.1	$\bar{3}$			< 0.8		13		< 0.5		11		1.1		12		< 0.6
6			4.3	$\bar{4}$			11.6	$\bar{4}$			0.9		14		5.8	8	1	0	2.3		13		< 0.6
7			5.7	$\bar{5}$			13.0	$\bar{5}$			0.7		15		3.3		2		1.4		14		2.4
1	0	4	10.2	$\bar{6}$			9.8	$\bar{6}$			0.9	4	1	0	19.2		3		2.2		15		3.3
2			7.0	$\bar{7}$			4.6	$\bar{7}$			2.6		2		2.0		4		3.2		16		2.2
3			5.7	$\bar{8}$			2.1	$\bar{8}$			6.7		3		8.7		5		1.4	$\bar{4}$	1	0	2.0
4			4.8	$\bar{9}$			< 0.8	$\bar{9}$			2.9		4		11.4		6		< 0.4		2		5.6
5			2.2	$\bar{10}$			2.3	$\bar{1}$	0	10	< 2.4		5		11.3		7		1.2		3		7.1
6			0.9	$\bar{11}$			3.6	$\bar{2}$			2.9		6		5.0		8		2.7		4		3.3
1	0	5	5.1	$\bar{12}$			< 2.2	$\bar{3}$			2.3		7		3.2	9	1	0	< 0.4		5		2.5
2			3.2	$\bar{13}$			1.6	$\bar{4}$			< 2.2		8		6.4		2		< 0.4		6		1.2
3			< 0.8	$\bar{1}$	0	5	13.6	$\bar{5}$			< 2.2		9		< 0.6		3		5.0		7		< 0.6
4			< 0.8	$\bar{2}$			3.2	$\bar{6}$			< 2.2		10		6.2		4		< 0.3		8		17.0
5			1.7	$\bar{3}$			5.3	$\bar{7}$			2.3		11		2.7		5		4.9		9		6.8
6			3.6	$\bar{4}$			3.9	$\bar{8}$			< 2.2		12		< 0.5	$\bar{1}$	1	0	12.8		10		5.3
1	0	6	1.1	$\bar{5}$			8.3	$\bar{9}$			< 2.3		13		< 0.5		2		1.6		11		9.5
2			0.9	$\bar{6}$			< 0.8	$\bar{10}$			1.0		14		1.2		3		16.3		12		< 0.6
3			0.9	$\bar{7}$			11.2	1	1	0	18.2		15		2.2		4		16.7		13		4.6
4			2.8	$\bar{8}$			4.9		2		13.8		16		< 2.4		5		19.4		14		1.5
5			2.0	$\bar{9}$			< 0.8		3		29.0		17		< 2.4		6		5.9		15		3.6
1	0	7	5.1	$\bar{10}$			3.3		4		1.3		18		3.2		7		2.6	$\bar{5}$	1	0	6.9
2			3.4	$\bar{11}$			1.8		5		13.0	5	1	0	1.6		8		5.2		2		0.7
3			3.1	$\bar{12}$			< 2.4		6		16.8		2		3.1		9		< 0.5		3		0.6
1	0	8	< 2.2	$\bar{13}$			2.5		7		4.5		3		2.6		10		4.7		4		3.0
2			2.0	$\bar{1}$	0	6	1.4		8		7.7		4		9.7		11		5.1		5		3.4
3			1.8	$\bar{2}$			1.1		9		3.4		5		2.1		12		2.5		6		5.1
$\bar{1}$	0	1	< 1.0	$\bar{3}$			6.7		10		3.8		6		5.2		13		6.2		7		2.7
$\bar{2}$			29.0	$\bar{4}$			3.3		11		2.1		7		2.2		14		7.4		8		3.5
$\bar{3}$			11.4	$\bar{5}$			5.1		12		1.8		8		3.1		15		< 0.5		9		1.4
$\bar{4}$			4.1	$\bar{6}$			5.0		13		4.2		9		0.9		16		< 0.5		10		4.6
$\bar{5}$			6.5	$\bar{7}$			2.7		14		4.8		10		1.9		17		< 2.4		11		4.2
$\bar{6}$			2.3	$\bar{8}$			1.9		15		1.9		11		2.8		18		6.4		12		1.3
$\bar{7}$			5.3	$\bar{9}$			5.2		16		< 0.3		12		2.5	$\bar{2}$	1	0	23.9		13		2.5
$\bar{8}$			7.8	$\bar{10}$			2.7	2	1	0	21.1		13		1.8		2		3.7		14		2.9
$\bar{9}$			< 0.6	$\bar{11}$			3.4		2		31.8		14		2.8		3		13.2		15		< 2.4
$\bar{10}$			1.5	$\bar{1}$	0	7	< 0.7		3		17.0		15		2.5		4		3.3		16		3.8
$\bar{1}$	0	2	29.6	$\bar{2}$			5.0		4		0.8	6	1	0	9.4		5		7.6	$\bar{6}$	1	0	3.7
$\bar{2}$			18.5	$\bar{3}$			< 0.7		5		12.8		2		11.2		6		13.7		2		7.3
$\bar{3}$			3.9	$\bar{4}$			3.9		6		3.4		3		6.3		7		3.6		3		2.9
$\bar{4}$			7.9	$\bar{5}$			3.3		7		5.2		4		4.8		8		1.1		4		8.3
$\bar{5}$			2.5	$\bar{6}$			2.6		8		1.7		5		< 0.6		9		6.2		5		2.8
$\bar{6}$			5.1	$\bar{7}$			5.1		9		1.0		6		9.8		10		< 0.6		6		7.6
$\bar{7}$			2.5	$\bar{8}$			1.5		10		3.5		7		9.1		11		6.6		7		1.5

h	k	l	Fo
$\bar{6}$	8	0	1.1
	9		0.7
	10		5.4
	11		< 0.5
	12		2.3
	13		1.7
$\bar{7}$	1	0	4.7
	2		4.0
	3		8.0
	4		4.1
	5		2.8
	6		5.6
	7		2.2
	8		0.8
	9		2.2
	10		0.9
	11		1.0
	12		2.9
	13		< 2.4
	14		3.5
$\bar{8}$	1	0	1.4
	2		2.0
	3		3.5
	4		< 0.5
	5		2.9
	6		2.5
	7		3.6
	8		2.5
	9		< 0.3
	10		< 0.2
$\bar{9}$	1	0	2.4
	2		2.4
	3		3.0
	4		5.9
	5		1.7
	6		< 0.2
	7		< 0.1
$\bar{10}$	1	0	2.6
	2		3.7
	3		< 2.4
	4		3.1
	5		2.7
	6		3.0
	7		3.8
	8		4.8
	9		4.9
1	1	1	5.7
	2		23.2
	3		25.0
	4		3.4
	5		4.5
	6		6.9
2	1	1	18.4
	2		27.9
	3		6.6
	4		20.3
	5		6.4
	6		4.0
	7		2.3
3	1	1	21.1
	2		1.7

h	k	l	Fo
3	3	1	13.3
	4		18.3
	5		4.4
	6		< 1.0
	7		2.6
	8		8.9
4	1	1	1.1
	2		3.0
	3		1.0
	4		12.1
	5		2.1
	6		< 1.1
	7		2.9
	8		1.2
5	1	1	2.4
	2		2.4
	3		6.6
	4		1.9
	5		6.1
	6		2.3
	7		2.4
6	1	1	4.3
	2		6.5
	3		3.6
	4		8.0
	5		2.4
	6		1.9
	7		< 1.1
	8		< 1.0
7	1	1	1.8
	2		3.4
	3		< 1.1
	4		2.2
	5		< 1.0
	6		< 1.0
	7		5.2
8	1	1	2.5
	2		1.4
	3		1.8
	4		2.9
	5		2.3
9	1	1	1.6
	2		< 0.4
1	$\bar{1}$	1	5.5
	$\bar{2}$		13.7
	$\bar{3}$		1.0
	$\bar{4}$		7.1
	$\bar{5}$		4.7
	$\bar{6}$		< 0.8
	$\bar{7}$		4.8
	$\bar{8}$		8.9
	$\bar{9}$		3.6
	$\bar{10}$		3.6
	$\bar{11}$		3.1
	$\bar{12}$		< 1.2
	$\bar{13}$		< 1.2
	$\bar{14}$		< 1.1
	$\bar{15}$		6.2
	$\bar{16}$		2.6
2	$\bar{1}$	1	3.1
	$\bar{2}$		3.3

h	k	l	Fo
2	$\bar{3}$	1	21.0
	$\bar{4}$		5.9
	$\bar{5}$		15.5
	$\bar{6}$		2.2
	$\bar{7}$		7.9
	$\bar{8}$		10.6
	$\bar{9}$		7.8
	$\bar{10}$		4.4
	$\bar{11}$		8.9
	$\bar{12}$		7.3
	$\bar{13}$		3.6
	$\bar{14}$		6.1
	$\bar{15}$		4.1
	$\bar{16}$		< 0.7
3	$\bar{1}$	1	7.7
	$\bar{2}$		5.7
	$\bar{3}$		22.2
	$\bar{4}$		23.5
	$\bar{5}$		14.4
	$\bar{6}$		2.8
	$\bar{7}$		5.1
	$\bar{8}$		4.1
	$\bar{9}$		< 1.1
	$\bar{10}$		12.8
	$\bar{11}$		4.4
	$\bar{12}$		8.0
	$\bar{13}$		1.7
	$\bar{14}$		3.9
	$\bar{15}$		2.8
	$\bar{16}$		< 0.5
4	$\bar{1}$	1	1.6
	$\bar{2}$		4.3
	$\bar{3}$		4.9
	$\bar{4}$		1.2
	$\bar{5}$		8.6
	$\bar{6}$		1.5
	$\bar{7}$		4.1
	$\bar{8}$		4.8
	$\bar{9}$		8.1
	$\bar{10}$		8.5
	$\bar{11}$		4.0
	$\bar{12}$		3.5
	$\bar{13}$		1.6
	$\bar{14}$		2.4
5	$\bar{1}$	1	3.7
	$\bar{2}$		1.8
	$\bar{3}$		1.9
	$\bar{4}$		< 1.1
	$\bar{5}$		1.6
	$\bar{6}$		4.3
	$\bar{7}$		5.0
	$\bar{8}$		5.9
	$\bar{9}$		1.9
	$\bar{10}$		1.9
	$\bar{11}$		< 1.1
	$\bar{12}$		< 1.0
	$\bar{13}$		4.3
	$\bar{14}$		3.4
6	$\bar{1}$	1	6.1
	$\bar{2}$		1.8
	$\bar{3}$		9.4

h	k	l	Fo
6	$\bar{4}$	1	3.1
	$\bar{5}$		3.3
	$\bar{6}$		2.0
	$\bar{7}$		11.8
	$\bar{8}$		< 1.1
	$\bar{9}$		1.9
	$\bar{10}$		< 1.1
	$\bar{11}$		< 0.9
	$\bar{12}$		2.5
	$\bar{13}$		2.8
7	$\bar{1}$	1	7.7
	$\bar{2}$		< 1.2
	$\bar{3}$		< 1.2
	$\bar{4}$		3.7
	$\bar{5}$		< 1.1
	$\bar{6}$		< 1.1
	$\bar{7}$		3.3
	$\bar{8}$		< 0.9
	$\bar{9}$		< 0.9
	$\bar{10}$		1.3
	$\bar{11}$		1.0
8	$\bar{1}$	1	< 1.0
	$\bar{2}$		2.6
	$\bar{3}$		< 0.9
	$\bar{4}$		3.6
	$\bar{5}$		2.9
	$\bar{6}$		< 0.8
	$\bar{7}$		1.2
	$\bar{8}$		1.1
9	$\bar{1}$	1	< 0.5
	$\bar{2}$		1.4
	$\bar{3}$		2.1
$\bar{1}$	1	1	26.6
	2		31.8
	3		39.0
	4		17.1
	5		29.5
	6		3.1
	7		7.1
	8		10.0
	9		4.7
	10		1.6
	11		4.4
$\bar{2}$	1	1	26.1
	2		3.4
	3		< 0.6
	4		5.8
	5		6.1
	6		2.4
	7		7.1
	8		3.4
	9		< 1.1
	10		5.0
	11		< 1.2
	12		3.4
$\bar{3}$	1	1	14.7
	2		4.3
	3		12.6
	4		8.6
	5		2.3
	6		10.0

h	k	l	Fo
$\bar{5}$	7	1	5.3
	8		5.8
	9		< 11
	10		5.5
	11		5.1
	12		< 1.2
	13		2.8
$\bar{4}$	1	1	11.5
	2		22.4
	3		22.4
	4		16.5
	5		9.4
	6		4.3
	7		10.5
	8		15.6
	9		11.6
	10		5.3
	11		< 1.2
	12		< 1.1
	13		< 1.0
$\bar{5}$	1	1	1.6
	2		< 1.0
	3		< 1.0
	4		< 1.0
	5		2.2
	6		1.5
	7		3.0
	8		3.4
	9		6.9
	10		< 1.2
	11		4.0
	12		< 1.0
	13		< 1.0
$\bar{6}$	1	1	11.9
	2		< 1.1
	3		10.0
	4		2.8
	5		2.5
	6		3.0
	7		3.8
	8		< 1.2
	9		7.2
	10		< 1.1
	11		< 1.0
	12		< 0.9
	13		< 0.8
$\bar{7}$	1	1	15.3
	2		5.2
	3		7.2
	4		5.6
	5		< 1.1
	6		5.2
	7		4.3
	8		3.9
	9		5.6
	10		3.9
	11		5.6
	12		3.3
$\bar{8}$	1	1	4.0
	2		3.2
	3		< 1.1

h	k	l	Fo
$\bar{8}$	4	1	< 1.1
	5		< 1.1
	6		3.8
	7		< 1.0
	8		< 0.9
	9		< 0.8
	10		< 0.6
$\bar{9}$	1	1	< 1.0
	2		1.7
	3		3.2
	4		3.3
	5		1.7
	6		< 0.8
	7		< 0.7
	8		1.1
$\bar{10}$	1	1	< 0.5
	2		5.0
	3		< 0.3
$\bar{1}$	$\bar{1}$	1	29.0
	$\bar{2}$		17.6
	$\bar{3}$		1.2
	$\bar{4}$		7.7
	$\bar{5}$		7.1
	$\bar{6}$		15.4
	$\bar{7}$		9.8
	$\bar{8}$		4.7
	$\bar{9}$		6.6
	$\bar{10}$		6.0
	$\bar{11}$		2.8
	$\bar{12}$		< 1.2
	$\bar{13}$		< 1.2
	$\bar{14}$		6.5
	$\bar{15}$		1.7
	$\bar{16}$		1.6
$\bar{2}$	$\bar{1}$	1	9.5
	$\bar{2}$		28.8
	$\bar{3}$		6.7
	$\bar{4}$		19.2
	$\bar{5}$		1.6
	$\bar{6}$		< 0.7
	$\bar{7}$		4.7
	$\bar{8}$		1.2
	$\bar{9}$		6.7
	$\bar{10}$		10.5
	$\bar{11}$		10.6
	$\bar{12}$		2.8
	$\bar{13}$		2.8
	$\bar{14}$		1.8
	$\bar{15}$		2.7
	$\bar{16}$		3.3
$\bar{3}$	$\bar{1}$	1	3.0
	$\bar{2}$		28.6
	$\bar{3}$		10.5
	$\bar{4}$		2.6
	$\bar{5}$		9.6
	$\bar{6}$		3.0
	$\bar{7}$		6.6
	$\bar{8}$		1.8
	$\bar{9}$		8.1
	$\bar{10}$		16.8
	$\bar{11}$		2.1

h	k	l	F_o	h	k	l	F_o	h	k	l	F_o	h	k	l	F_o	h	k	l	F_o	h	k	l	F_o
$\bar{3}$	$\bar{12}$	1	8.2	$\bar{8}$	$\bar{3}$	1	5.6	7	7	2	< 0.6	4	$\bar{12}$	2	< 1.0	$\bar{2}$	6	2	5.6	$\bar{7}$	1	2	2.8
	$\bar{13}$		2.6		$\bar{4}$		< 1.1	8	1	2	3.2		$\bar{13}$		< 0.9		7		2.7		2		1.5
	$\bar{14}$		< 1.0		$\bar{5}$		2.0		2		1.9		$\bar{14}$		2.3		8		3.1		3		1.7
	$\bar{15}$		< 0.8		$\bar{6}$		4.1	1	$\bar{1}$	2	1.5		$\bar{15}$		< 0.2		9		2.7		4		6.2
	$\bar{16}$		2.8		$\bar{7}$		3.3		$\bar{2}$		6.8	5	$\bar{1}$	2	3.0		10		3.2		5		10.8
$\bar{4}$	$\bar{1}$	1	3.7		$\bar{8}$		2.3		$\bar{3}$		4.9		$\bar{2}$		10.9		11		4.0		6		< 1.1
	$\bar{2}$		16.1		$\bar{9}$		< 0.7		$\bar{4}$		10.9		$\bar{3}$		4.4		12		4.8		7		< 1.1
	$\bar{3}$		19.7		$\bar{10}$		< 0.5		$\bar{5}$		18.9		$\bar{4}$		6.2	$\bar{3}$	1	2	2.0		8		2.7
	$\bar{4}$		3.1	$\bar{9}$	$\bar{1}$	1	< 0.9		$\bar{6}$		11.3		$\bar{5}$		4.2		2		1.6		9		4.7
	$\bar{5}$		< 0.9		$\bar{2}$		< 0.9		$\bar{7}$		3.4		$\bar{6}$		5.4		3		7.0		10		2.2
	$\bar{6}$		5.7		$\bar{3}$		< 0.9		$\bar{8}$		< 1.0		$\bar{7}$		< 1.1		4		6.2		11		1.6
	$\bar{7}$		2.9		$\bar{4}$		3.5		$\bar{9}$		2.6		$\bar{8}$		5.3		5		9.7		12		4.8
	$\bar{8}$		6.0		$\bar{5}$		< 0.8		$\bar{10}$		< 1.1		$\bar{9}$		< 1.1		6		5.6	$\bar{8}$	1	2	< 1.1
	$\bar{9}$		6.2		$\bar{6}$		< 0.7		$\bar{11}$		5.7		$\bar{10}$		< 1.0		7		7.2		2		2.9
	$\bar{10}$		3.1		$\bar{7}$		< 0.6		$\bar{12}$		9.6		$\bar{11}$		1.7		8		6.3		3		< 1.1
	$\bar{11}$		6.4	$\bar{10}$	$\bar{1}$	1	2.9		$\bar{13}$		2.1		$\bar{12}$		3.5		9		7.4		4		2.9
	$\bar{12}$		2.7		$\bar{2}$		< 0.4		$\bar{14}$		2.5		$\bar{13}$		< 0.7		10		3.3		5		5.9
	$\bar{13}$		2.5	1	1	2	18.7		$\bar{15}$		4.7	6	$\bar{1}$	2	3.4		11		1.7		6		3.5
	$\bar{14}$		1.5		2		17.3		$\bar{16}$		4.4		$\bar{2}$		3.2		12		< 1.1		7		< 1.0
	$\bar{15}$		4.2		3		9.8	2	$\bar{1}$	2	9.0		$\bar{3}$		3.0		13		3.1		8		2.2
$\bar{5}$	$\bar{1}$	1	7.0		4		3.6		$\bar{2}$		14.8		$\bar{4}$		4.6		14		< 0.9		9		1.5
	$\bar{2}$		3.5		5		6.7		$\bar{3}$		10.8		$\bar{5}$		2.9		15		< 0.7		10		4.1
	$\bar{3}$		5.1	2	1	2	5.7		$\bar{4}$		5.8		$\bar{6}$		1.9	$\bar{4}$	1	2	2.1	$\bar{9}$	1	2	2.3
	$\bar{4}$		3.9		2		14.1		$\bar{5}$		7.5		$\bar{7}$		< 1.1		2		30.9		2		1.6
	$\bar{5}$		15.2		3		13.3		$\bar{6}$		1.9		$\bar{8}$		3.0		3		1.4		3		2.5
	$\bar{6}$		3.0		4		3.3		$\bar{7}$		1.4		$\bar{9}$		< 0.9		4		2.1		4		< 0.9
	$\bar{7}$		3.8		5		3.5		$\bar{8}$		1.6		$\bar{10}$		2.5		5		3.7		5		< 0.8
	$\bar{8}$		3.1		6		8.5		$\bar{9}$		1.9		$\bar{11}$		< 0.7		6		11.7		6		< 0.9
	$\bar{9}$		6.4	3	1	2	1.3		$\bar{10}$		11.7		$\bar{12}$		1.1		7		5.1		7		1.1
	$\bar{10}$		1.8		2		11.7		$\bar{11}$		5.7	7	$\bar{1}$	2	4.2		8		5.5		8		1.1
	$\bar{11}$		3.0		3		5.9		$\bar{12}$		2.1		$\bar{2}$		< 1.0		9		8.4	$\bar{10}$	1	2	1.7
	$\bar{12}$		< 1.0		4		7.8		$\bar{13}$		1.6		$\bar{3}$		< 1.0		10		8.0		2		2.5
	$\bar{13}$		< 0.9		5		2.4		$\bar{14}$		< 1.0		$\bar{4}$		< 1.0		11		3.0		3		< 0.7
	$\bar{14}$		2.0		6		< 1.1		$\bar{15}$		4.9		$\bar{5}$		2.3		12		1.7		4		4.2
$\bar{6}$	$\bar{1}$	1	11.3		7		9.5		$\bar{16}$		< 0.6		$\bar{6}$		4.5		13		1.6		5		1.4
	$\bar{2}$		3.5	4	1	2	< 1.0	3	$\bar{1}$	2	5.6		$\bar{7}$		< 0.8	$\bar{5}$	1	2	9.5		6		< 0.3
	$\bar{3}$		4.4		2		2.1		$\bar{2}$		5.3		$\bar{8}$		2.4		2		4.7	$\bar{1}$	$\bar{1}$	2	5.7
	$\bar{4}$		5.3		3		4.3		$\bar{3}$		4.9		$\bar{9}$		< 1.0		3		11.1		$\bar{2}$		27.5
	$\bar{5}$		1.9		4		< 1.1		$\bar{4}$		11.1		$\bar{10}$		1.2		4		< 1.0		$\bar{3}$		1.3
	$\bar{6}$		1.8		5		< 1.1		$\bar{5}$		4.8	8	$\bar{1}$	2	1.8		5		6.4		$\bar{4}$		17.3
	$\bar{7}$		2.1		6		< 1.1		$\bar{6}$		1.3		$\bar{2}$		< 0.7		6		2.3		$\bar{5}$		7.7
	$\bar{8}$		5.1		7		3.5		$\bar{7}$		< 1.1		$\bar{3}$		2.3		7		4.4		$\bar{6}$		10.2
	$\bar{9}$		5.6	5	1	2	4.0		$\bar{8}$		4.6		$\bar{4}$		< 0.7		8		7.3		$\bar{7}$		6.0
	$\bar{10}$		3.7		2		5.0		$\bar{9}$		1.9		$\bar{5}$		1.9		9		7.7		$\bar{8}$		10.0
	$\bar{11}$		< 1.0		3		4.2		$\bar{10}$		7.0		$\bar{6}$		< 0.5		10		3.5		$\bar{9}$		6.3
	$\bar{12}$		< 0.9		4		1.5		$\bar{11}$		1.7	$\bar{1}$	1	2	3.4		11		1.3		$\bar{10}$		2.7
	$\bar{13}$		3.1		5		1.5		$\bar{12}$		3.6		2		7.2		12		[illegible]		$\bar{11}$		6.0
$\bar{7}$	$\bar{1}$	1	11.3		6		7.6		$\bar{13}$		< 1.0		3		6.2		13		3.2		$\bar{12}$		4.9
	$\bar{2}$		12.4	6	1	2	6.8		14		1.5		4		7.8	$\bar{6}$	1	2	< 1.0		$\bar{13}$		2.9
	$\bar{3}$		1.5		2		< 1.1		15		1.3		5		25.2		2		10.6		$\bar{14}$		< 1.1
	$\bar{4}$		4.0		3		5.3	4	$\bar{1}$	2	11.1		6		13.8		3		< 1.1		$\bar{15}$		3.1
	$\bar{5}$		< 1.2		4		< 1.1		$\bar{2}$		6.2		7		3.9		4		5.6		$\bar{16}$		2.6
	$\bar{6}$		3.6		5		< 1.1		$\bar{3}$		5.2		8		2.6		5		2.9		$\bar{17}$		4.3
	$\bar{7}$		1.8		6		< 1.0		$\bar{4}$		8.7		9		2.3		6		7.8	$\bar{2}$	$\bar{1}$	2	8.8
	$\bar{8}$		4.2		7		< 0.9		$\bar{5}$		< 1.1		10		6.4		7		2.9		$\bar{2}$		21.6
	$\bar{9}$		< 1.0	7	1	2	1.9		$\bar{6}$		2.5		11		2.4		8		3.2		$\bar{3}$		18.0
	$\bar{10}$		< 0.9		2		< 1.0		$\bar{7}$		6.8	$\bar{2}$	1	2	15.2		9		< 1.1		$\bar{4}$		18.2
	$\bar{11}$		< 0.8		3		6.0		$\bar{8}$		< 1.1		2		5.8		10		1.6		$\bar{5}$		8.9
	$\bar{12}$		< 0.5		4		< 0.9		$\bar{9}$		< 1.1		3		2.5		11		1.9		$\bar{6}$		8.1
$\bar{8}$	$\bar{1}$	1	7.5		5		< 0.8		$\bar{10}$		< 1.1		4		14.8		12		1.9		$\bar{7}$		26.6
	$\bar{2}$		5.3		6		< 0.7		$\bar{11}$		9.2		5		3.8		13		2.2		$\bar{8}$		4.0

h	k	l	F_o	h	k	l	F_o	h	k	l	F_o	h	k	l	F_o	h	k	l	F_o	h	k	l	F_o
$\bar{2}$	$\bar{9}$	2	2.5	$\bar{6}$	$\bar{8}$	2	5.7	3	6	3	< 1.2	3	$\bar{11}$	3	5.8	$\bar{2}$	3	3	2.6	$\bar{6}$	13	3	1.0
	$\bar{10}$		7.5		$\bar{9}$		2.7	4	1	3	6.5		$\bar{12}$		3.1		4		0.8	$\bar{7}$	1	3	5.1
	$\bar{11}$		8.0		$\bar{10}$		3.4		2		< 1.2		$\bar{13}$		1.3		5		10.4		2		3.3
	$\bar{12}$		4.8		$\bar{11}$		4.3		3		2.6		$\bar{14}$		1.9		6		5.0		3		< 1.2
	$\bar{13}$		< 1.1		$\bar{12}$		< 0.9		4		< 1.3		$\bar{15}$		1.5		7		8.7		4		6.1
	$\bar{14}$		< 1.1		$\bar{13}$		4.9		5		5.5	4	$\bar{1}$	3	7.0		8		1.7		5		< 1.2
	$\bar{15}$		< 0.9		$\bar{14}$		3.4	5	1	3	< 1.2		$\bar{2}$		1.4		9		2.0		6		4.5
	$\bar{16}$		< 0.7	$\bar{7}$	$\bar{1}$	2	8.7		2		1.2		$\bar{3}$		13.1		10		2.7		7		2.3
$\bar{3}$	$\bar{1}$	2	8.1		$\bar{2}$		4.2		3		1.6		$\bar{4}$		< 1.2		11		2.0		8		5.1
	$\bar{2}$		21.6		$\bar{3}$		4.8		4		< 1.2		$\bar{5}$		2.9		12		8.0		9		1.5
	$\bar{3}$		17.3		$\bar{4}$		4.6		5		< 1.2		$\bar{6}$		1.2	$\bar{3}$	1	3	5.8		10		2.9
	$\bar{4}$		7.2		$\bar{5}$		< 1.1		6		< 1.2		$\bar{7}$		5.0		2		1.8		11		2.0
	$\bar{5}$		2.4		$\bar{6}$		5.9	6	1	3	1.2		$\bar{8}$		< 1.2		3		17.6		12		< 0.5
	$\bar{6}$		6.3		$\bar{7}$		2.3		2		3.2		$\bar{9}$		2.7		4		< 1.0	$\bar{8}$	1	3	1.4
	$\bar{7}$		5.5		$\bar{8}$		2.3		3		< 1.2		$\bar{10}$		5.7		5		4.3		2		1.6
	$\bar{8}$		5.2		$\bar{9}$		< 1.0		4		< 1.1		$\bar{11}$		2.5		6		4.6		3		5.8
	$\bar{9}$		9.2		$\bar{10}$		< 1.0		5		< 1.0		$\bar{12}$		3.9		7		3.7		4		5.6
	$\bar{10}$		1.7		$\bar{11}$		2.1	7	1	3	< 0.8		$\bar{13}$		2.0		8		< 1.2		5		1.3
	$\bar{11}$		8.9		$\bar{12}$		1.3		2		< 0.8		$\bar{14}$		1.0		9		1.8		6		2.8
	$\bar{12}$		5.1		$\bar{13}$		0.3	1	$\bar{1}$	3	4.9	5	$\bar{1}$	3	5.2		10		< 1.3		7		3.6
	$\bar{13}$		1.8	$\bar{8}$	$\bar{1}$	2	< 1.1		$\bar{2}$		12.6		$\bar{2}$		9.6		11		< 1.2		8		1.5
	$\bar{14}$		1.6		$\bar{2}$		1.9		$\bar{3}$		2.6		$\bar{3}$		< 1.2		12		2.7		9		< 0.8
	$\bar{15}$		< 0.9		$\bar{3}$		4.5		$\bar{4}$		8.7		$\bar{4}$		< 1.2		13		2.0		10		3.1
	$\bar{16}$		< 0.6		$\bar{4}$		3.5		$\bar{5}$		1.7		$\bar{5}$		< 1.2	$\bar{4}$	1	3	8.4	$\bar{9}$	1	3	2.6
$\bar{4}$	$\bar{1}$	2	8.0		$\bar{5}$		< 1.1		$\bar{6}$		4.3		$\bar{6}$		5.4		2		3.2		2		< 1.2
	$\bar{2}$		7.4		$\bar{6}$		< 1.1		$\bar{7}$		4.6		$\bar{7}$		< 1.2		3		8.6		3		3.7
	$\bar{3}$		17.5		$\bar{7}$		1.9		$\bar{8}$		7.6		$\bar{8}$		3.1		4		6.5		4		< 1.1
	$\bar{4}$		2.8		$\bar{8}$		4.0		$\bar{9}$		12.7		$\bar{9}$		2.7		5		12.4		5		4.4
	$\bar{5}$		13.1		$\bar{9}$		1.4		$\bar{10}$		8.1		$\bar{10}$		< 1.0		6		< 1.2		6		2.0
	$\bar{6}$		9.6		$\bar{10}$		1.2		$\bar{11}$		9.9		$\bar{11}$		1.2		7		6.5		7		1.7
	$\bar{7}$		3.0		$\bar{11}$		< 0.6		$\bar{12}$		3.9		$\bar{12}$		2.0		8		< 1.2		8		< 0.6
	$\bar{8}$		4.7	$\bar{9}$	$\bar{1}$	2	5.4		$\bar{13}$		< 1.2	6	$\bar{1}$	3	4.4		9		7.4	$\bar{10}$	1	3	2.1
	$\bar{9}$		< 1.1		$\bar{2}$		< 1.0		$\bar{14}$		7.1		$\bar{2}$		2.6		10		3.8		2		< 0.8
	$\bar{10}$		8.3		$\bar{3}$		2.4		$\bar{15}$		1.9		$\bar{3}$		5.6		11		< 1.2		3		4.9
	$\bar{11}$		7.0		$\bar{4}$		< 0.9		$\bar{16}$		1.2		$\bar{4}$		2.9		12		1.7		4		1.0
	$\bar{12}$		2.7		$\bar{5}$		1.3	2	$\bar{1}$	3	5.6		$\bar{5}$		< 1.2		13		1.7		6		1.7
	$\bar{13}$		< 1.0		$\bar{6}$		3.6		$\bar{2}$		6.1		$\bar{6}$		3.0	$\bar{5}$	1	3	4.6	$\bar{1}$	$\bar{1}$	3	15.0
	$\bar{14}$		< 0.9		$\bar{7}$		< 0.7		$\bar{3}$		7.6		$\bar{7}$		3.0		2		1.3		$\bar{2}$		30.6
	$\bar{15}$		< 0.7		$\bar{8}$		1.0		$\bar{4}$		5.8		$\bar{8}$		3.0		3		1.9		$\bar{3}$		7.9
	$\bar{16}$		< 0.4		$\bar{9}$		< 0.2		$\bar{5}$		< 1.1		$\bar{9}$		< 0.8		4		6.4		$\bar{4}$		2.3
$\bar{5}$	$\bar{1}$	2	1.2	$\bar{10}$	$\bar{1}$	2	< 0.7		$\bar{6}$		10.4		$\bar{10}$		< 0.7		5		< 1.2		$\bar{5}$		4.6
	$\bar{2}$		9.2		$\bar{2}$		3.5		$\bar{7}$		6.1	7	$\bar{1}$	3	< 0.8		6		10.1		$\bar{6}$		6.3
	$\bar{3}$		4.7		$\bar{3}$		1.8		$\bar{8}$		4.0		$\bar{2}$		3.9		7		13.9		$\bar{7}$		5.0
	$\bar{4}$		12.1		$\bar{4}$		1.6		$\bar{9}$		3.9		$\bar{3}$		2.3		8		6.8		$\bar{8}$		5.4
	$\bar{5}$		5.1		$\bar{5}$		2.2		$\bar{10}$		8.2		$\bar{4}$		3.8		9		9.9		$\bar{9}$		4.6
	$\bar{6}$		5.2	1	1	3	8.4		$\bar{11}$		4.0		$\bar{5}$		2.3		10		1.7		$\bar{10}$		3.7
	$\bar{7}$		< 1.1		2		11.8		$\bar{12}$		1.5		$\bar{6}$		1.5		11		3.1		$\bar{11}$		< 1.2
	$\bar{8}$		2.4		3		1.2		$\bar{13}$		5.0		$\bar{7}$		< 0.5		12		2.4		$\bar{12}$		3.6
	$\bar{9}$		< 1.1		4		5.6		$\bar{14}$		2.9	$\bar{1}$	1	3	3.8		13		4.2		$\bar{13}$		< 1.2
	$\bar{10}$		4.7		5		1.5		$\bar{15}$		1.2		2		14.6	$\bar{6}$	1	3	2.0		$\bar{14}$		3.2
	$\bar{11}$		4.1	2	1	3	2.5		$\bar{16}$		< 0.2		3		6.2		2		8.9		$\bar{15}$		1.9
	$\bar{12}$		9.2		2		4.4	3	$\bar{1}$	3	8.6		4		15.1		3		3.7		$\bar{16}$		1.7
	$\bar{13}$		1.7		3		4.0		$\bar{2}$		3.9		5		8.4		4		2.7	$\bar{2}$	$\bar{1}$	3	22.2
	$\bar{14}$		2.3		4		6.5		$\bar{3}$		3.7		6		< 1.1		5		3.2		$\bar{2}$		30.1
$\bar{6}$	$\bar{1}$	2	9.0		5		< 1.2		$\bar{4}$		< 1.2		7		8.3		6		2.6		$\bar{3}$		30.9
	$\bar{2}$		5.1		6		< 1.2		$\bar{5}$		< 1.2		8		< 1.2		7		2.1		$\bar{4}$		6.1
	$\bar{3}$		5.4	3	1	3	8.7		$\bar{6}$		5.0		9		6.5		8		2.0		$\bar{5}$		10.9
	$\bar{4}$		< 1.1		2		3.0		$\bar{7}$		4.2		10		4.0		9		< 1.2		$\bar{6}$		2.6
	$\bar{5}$		< 1.1		3		1.9		$\bar{8}$		4.0		11		1.8		10		< 1.2		$\bar{7}$		2.7
	$\bar{6}$		8.8		4		2.9		$\bar{9}$		5.6	$\bar{2}$	1	3	3.6		11		2.7		$\bar{8}$		5.5
	$\bar{7}$		1.1		5		< 1.2		$\bar{10}$		3.3		2		5.6		12		1.3		$\bar{9}$		4.5

h	k	l	Fo	h	k	l	Fo	h	k	l	Fo	h	k	l	Fo	h	k	l	Fo	h	k	l	Fo
$\bar{2}$	$\bar{10}$	3	11.5	$\bar{6}$	$\bar{8}$	3	3.2	4	4	4	< 1.2	4	$\bar{11}$	4	< 0.9	$\bar{4}$	6	4	5.5	$\bar{9}$	8	4	1.9
	$\bar{11}$		4.2		$\bar{9}$		4.4	5	1	4	< 1.1		$\bar{12}$		2.3		7		8.4	$\bar{10}$	1	4	3.4
	$\bar{12}$		4.2		$\bar{10}$		6.2		2		1.2		$\bar{13}$		< 0.2		8		5.8		2		3.3
	$\bar{13}$		2.1		$\bar{11}$		7.1		3		< 1.0	5	$\bar{1}$	4	6.2		9		4.5		3		1.2
	$\bar{14}$		4.5		$\bar{12}$		1.4		4		< 1.0		$\bar{2}$		3.3		10		2.0		4		1.7
	$\bar{15}$		< 1.0		$\bar{13}$		2.6	6	1	4	< 0.9		$\bar{3}$		4.6		11		1.8		5		< 0.6
	$\bar{16}$		1.4		$\bar{16}$		3.0	1	$\bar{1}$	4	6.9		$\bar{4}$		< 1.1		12		4.6	$\bar{1}$	$\bar{1}$	4	11.9
$\bar{3}$	$\bar{1}$	3	7.4	$\bar{7}$	$\bar{1}$	3	9.6		$\bar{2}$		1.8		$\bar{5}$		2.2		13		1.7		$\bar{2}$		8.2
	$\bar{2}$		16.7		$\bar{2}$		< 1.2		$\bar{3}$		9.3		$\bar{6}$		< 1.0	$\bar{5}$	1	4	10.0		$\bar{3}$		27.3
	$\bar{3}$		7.3		$\bar{3}$		10.9		$\bar{4}$		2.0		$\bar{7}$		1.8		2		10.7		$\bar{4}$		4.8
	$\bar{4}$		2.5		$\bar{4}$		5.0		$\bar{5}$		15.9		$\bar{8}$		< 1.0		3		6.7		$\bar{5}$		1.6
	$\bar{5}$		13.7		$\bar{5}$		2.6		$\bar{6}$		4.5		$\bar{9}$		2.2		4		4.8		$\bar{6}$		2.2
	$\bar{6}$		17.7		$\bar{6}$		2.9		$\bar{7}$		6.7		$\bar{10}$		1.9		5		3.3		$\bar{7}$		< 1.0
	$\bar{7}$		4.9		$\bar{7}$		4.8		$\bar{8}$		< 1.2	6	$\bar{1}$	4	< 0.9		6		< 1.2		$\bar{8}$		< 1.0
	$\bar{8}$		9.2		$\bar{8}$		3.3		$\bar{9}$		7.9		$\bar{2}$		1.6		7		12.0		$\bar{9}$		6.0
	$\bar{9}$		2.1		$\bar{9}$		2.3		$\bar{10}$		10.0		$\bar{3}$		3.0		8		2.7		$\bar{10}$		5.1
	$\bar{10}$		< 1.2		$\bar{10}$		1.9		$\bar{11}$		< 1.2		$\bar{4}$		2.2		9		< 1.2		$\bar{11}$		5.6
	$\bar{11}$		6.8		$\bar{11}$		1.8		$\bar{12}$		3.2		$\bar{5}$		1.5		10		4.1		$\bar{12}$		2.4
	$\bar{12}$		< 1.2		$\bar{12}$		4.4		$\bar{13}$		5.2		$\bar{6}$		4.3		11		< 1.0		$\bar{13}$		2.7
	$\bar{13}$		4.3		$\bar{13}$		< 0.6		$\bar{14}$		4.3		$\bar{7}$		2.8		12		3.2		$\bar{14}$		1.2
	$\bar{14}$		< 1.2	$\bar{8}$	$\bar{1}$	3	9.3		$\bar{15}$		3.3		$\bar{8}$		2.0		13		1.0		$\bar{15}$		< 0.9
	$\bar{15}$		3.8		$\bar{2}$		8.2		$\bar{16}$		< 0.7	$\bar{1}$	1	4	12.3	$\bar{6}$	1	4	1.9		$\bar{16}$		< 0.6
	$\bar{16}$		< 0.7		$\bar{3}$		5.7	2	$\bar{1}$	4	6.0		2		9.2		2		3.1	$\bar{2}$	$\bar{1}$	4	NOT RECORDED
$\bar{4}$	$\bar{1}$	3	5.2		$\bar{4}$		2.3		$\bar{2}$		8.8		3		2.0		3		4.0		$\bar{2}$		2.9
	$\bar{2}$		9.2		$\bar{5}$		3.3		$\bar{3}$		2.5		4		7.3		4		4.6		$\bar{3}$		6.0
	$\bar{3}$		8.4		$\bar{6}$		1.2		$\bar{4}$		4.1		5		< 1.0		5		6.1		$\bar{4}$		2.8
	$\bar{4}$		13.8		$\bar{7}$		1.7		$\bar{5}$		11.0		6		8.2		6		6.0		$\bar{5}$		9.1
	$\bar{5}$		9.5		$\bar{8}$		3.3		$\bar{6}$		< 1.2		7		5.2		7		< 1.2		$\bar{6}$		3.1
	$\bar{6}$		< 1.0		$\bar{9}$		1.4		$\bar{7}$		5.3		8		6.2		8		2.7		$\bar{7}$		11.4
	$\bar{7}$		8.6		$\bar{10}$		3.5		$\bar{8}$		4.6		9		< 1.2		9		1.2		$\bar{8}$		13.8
	$\bar{8}$		< 1.2		$\bar{11}$		2.9		$\bar{9}$		5.7		10		< 1.2		10		3.0		$\bar{9}$		3.5
	$\bar{9}$		7.1	$\bar{9}$	$\bar{1}$	3	1.4		$\bar{10}$		3.6	$\bar{2}$	1	4	16.5		11		< 1.0		$\bar{10}$		1.6
	$\bar{10}$		5.4		$\bar{2}$		6.4		$\bar{11}$		2.9		2		2.3		12		3.6		$\bar{11}$		< 1.2
	$\bar{11}$		4.6		$\bar{3}$		2.9		$\bar{12}$		1.7		3		14.0	$\bar{7}$	1	4	2.1		$\bar{12}$		1.7
	$\bar{12}$		2.5		$\bar{4}$		4.2		$\bar{13}$		< 1.0		4		4.0		2		6.5		$\bar{13}$		< 1.2
	$\bar{13}$		1.9		$\bar{5}$		< 1.1		$\bar{14}$		3.5		5		< 1.0		3		2.9		$\bar{14}$		2.7
	$\bar{14}$		2.9		$\bar{6}$		6.8		$\bar{15}$		1.2		6		8.7		4		< 1.2		$\bar{15}$		2.4
	$\bar{15}$		< 0.8		$\bar{7}$		< 1.0	3	$\bar{1}$	4	6.9		7		< 1.2		5		1.4		$\bar{16}$		< 0.6
	$\bar{16}$		0.8		$\bar{8}$		1.9		$\bar{2}$		7.8		8		< 1.2		6		3.2	$\bar{3}$	$\bar{1}$	4	4.2
$\bar{5}$	$\bar{1}$	3	7.1		$\bar{9}$		1.3		$\bar{3}$		6.7		9		2.4		7		8.3		$\bar{2}$		35.0
	$\bar{2}$		4.4	$\bar{10}$	$\bar{1}$	3	1.9		$\bar{4}$		5.0		10		4.5		8		< 1.1		$\bar{3}$		4.0
	$\bar{3}$		9.4		$\bar{2}$		4.5		$\bar{5}$		< 1.2		11		5.7		9		< 1.0		$\bar{4}$		15.4
	$\bar{4}$		< 1.0		$\bar{3}$		< 0.8		$\bar{6}$		5.3		12		2.4		10		< 0.9		$\bar{5}$		15.1
	$\bar{5}$		3.0		$\bar{4}$		5.4		$\bar{7}$		3.6	$\bar{3}$	1	4	6.3		11		4.7		$\bar{6}$		7.4
	$\bar{6}$		5.5		$\bar{5}$		1.2		$\bar{8}$		2.1		2		4.0	$\bar{8}$	1	4	4.5		$\bar{7}$		1.4
	$\bar{7}$		9.9		$\bar{6}$		3.1		$\bar{9}$		1.6		3		2.6		2		4.7		$\bar{8}$		2.2
	$\bar{8}$		5.4	1	1	4	5.2		$\bar{10}$		3.5		4		14.6		3		1.6		$\bar{9}$		5.5
	$\bar{9}$		10.5		2		8.4		$\bar{11}$		4.6		5		6.8		4		< 1.2		$\bar{10}$		1.2
	$\bar{10}$		6.0		3		5.1		$\bar{12}$		< 1.0		6		4.8		5		1.6		$\bar{11}$		6.1
	$\bar{11}$		2.7		4		3.7		$\bar{13}$		2.6		7		< 1.2		6		3.8		$\bar{12}$		5.5
	$\bar{12}$		2.6	2	1	4	< 1.1		$\bar{14}$		< 0.5		8		1.4		7		1.6		$\bar{13}$		3.3
	$\bar{13}$		< 1.1		2		4.7	4	$\bar{1}$	4	5.5		9		2.2		8		5.5		$\bar{14}$		< 1.0
	$\bar{14}$		2.3		3		10.6		$\bar{2}$		9.9		10		3.1		9		1.7		$\bar{15}$		2.9
	$\bar{15}$		1.8		4		< 1.2		$\bar{3}$		2.8		11		6.1		10		< 0.5		$\bar{16}$		0.9
$\bar{6}$	$\bar{1}$	3	4.3	3	1	4	< 1.2		$\bar{4}$		1.4		12		1.4	$\bar{9}$	1	4	< 1.1	$\bar{4}$	$\bar{1}$	4	10.0
	$\bar{2}$		8.2		2		2.7		$\bar{5}$		4.0		13		< 0.9		2		2.8		$\bar{2}$		8.2
	$\bar{3}$		3.3		3		6.7		$\bar{6}$		1.7	$\bar{4}$	1	4	2.4		3		< 1.0		$\bar{3}$		20.1
	$\bar{4}$		5.1		4		6.3		$\bar{7}$		1.4		2		< 0.9		4		2.8		$\bar{4}$		3.0
	$\bar{5}$		4.0	4	1	4	2.9		$\bar{8}$		4.1		3		9.3		5		2.1		$\bar{5}$		4.6
	$\bar{6}$		6.5		2		2.5		$\bar{9}$		2.1		4		3.3		6		2.4		$\bar{6}$		9.7
	$\bar{7}$		6.3		3		3.8		$\bar{10}$		5.3		5		2.7		7		< 0.7		$\bar{7}$		2.6

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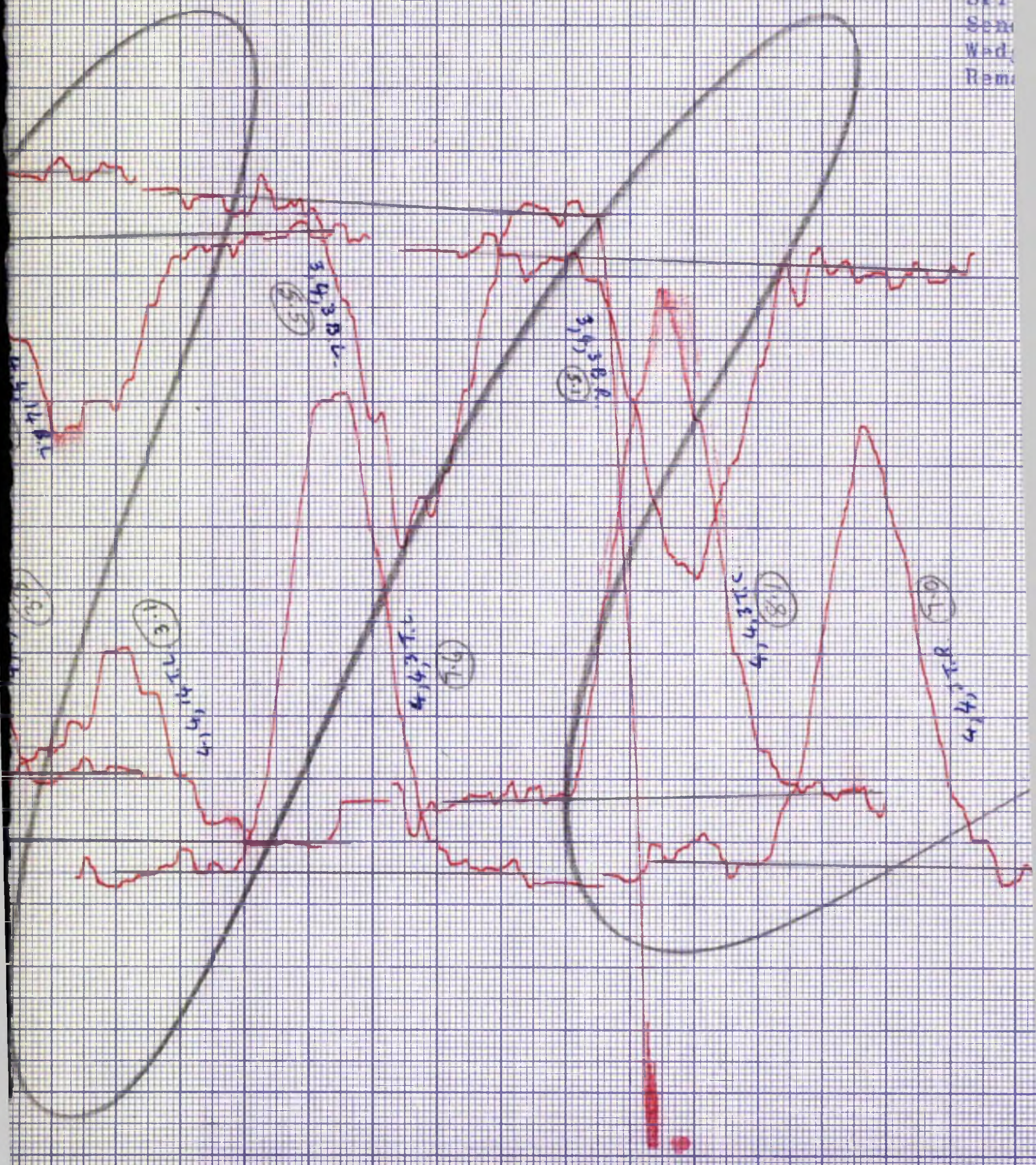

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