Refinement of the structure of anthraquinone*

By B. V. R. MURTY**

Physics Department, Allahabad University, Allahabad, India

With 8 figures

Auszug

Die Kristallstruktur von Anthrachinon wurde neu untersucht. Die Atomparameter sind zu einer Genauigkeit von $\pm$ 0,01 Å verfeinert worden. Es wurden zweidimensionale $(F_o–F_c)$-Synthesen und dreidimensionale F_o- und Differential-Synthesen ausgeführt. Die Lagen der Wasserstoffatome konnten angegeben und an Hand der Intensitäten bestätigt werden. Das Molekül, einschließlich aller H-Atome, ist eben. Die Genauigkeit der Analyse und der Atomabstände wird diskutiert.

Abstract

The crystal structure of anthraquinone has been reinvestigated and the atomic parameters have been refined to an accuracy of 0.01 Å. Two-dimensional $(F_o–F_c)$ synthesis, three-dimensional F_o synthesis and three-dimensional differential synthesis have been used. Hydrogen atoms are detected and their positions are verified. The molecule is planar with all the hydrogen atoms also lying in the same plane. Some data concerning the different atoms are given. The accuracy of the analysis and the bond lengths are discussed.

1. Introduction

The structure of anthraquinone, $C_{14}H_8O_2$, was determined by SEN[1] by two-dimensional Fourier synthesis. He[2] assigned the space group $P2_1/a$ but in his latter work[1] mentioned the observation of a few weak forbidden reflections ($h0l$ with h odd) which led him to ascribe $P2_1$

---

* The work formed a part of the thesis submitted for the D. Phil. degree of the Allahabad University.

** Formerly at the Indian Association for the Cultivation of Science, Jadavpur, Calcutta-32, India and now at the Applied Physics Department, Indian Institute of Technology, Madras, India.

[1] S. N. SEN, Crystal structure of anthraquinone, Thesis, Calcutta University (1948).

[2] S. N. SEN, Crystal structure of anthraquinone. Science and Culture 5 (1940) 717—719.

as the space group. The structure was worked out on the basis of $P2_1/a$ neglecting the contribution of these few, in fact only four, very weak forbidden reflections. F_c values were calculated by using the atomic form factor curves of benzoquinone carbon[3] and magnesium oxide oxygen[4]. Although general agreement between F_o and F_c appeared to be somewhat satisfactory, sharp differences between a few intense reflections were quite frequently observed, F_c being less in all these cases. The total electron count that was made for each atom gave a figure 9.5 for oxygen while for each of the other atoms it was about 6.0 including also the carbon atom that forms a double bond with oxygen. A partial ionic character of the oxygen atom was mentioned but the immediate question was wherefrom this extra value of 1.5 for oxygen could have been derived. Probable inaccuracies of the intensity measurements and the termination of Fourier series were thought to be responsible for this. It was thought worthwhile to settle these points of interest by a refinement of the structure by the application of three-dimensional Fourier methods.

The author has in his earlier publications[5,6] established that the space group of anthraquinone is $P2_1/a$ and the scattering factors appropriate to the different atoms of the substance at room temperature (at which this present analysis was done) were determined by an empirical method developed by him. The refinement of the structure is dealt with in this article.

2. Crystal data

Anthraquinone, $C_{14}H_8O_2$; melting point $273\,°C$; density measured 1.438, calculated 1.445; monoclinic; revised unit-cell dimensions, $a = 15.810 \pm 0.015\ Å$, $b = 3.942 \pm 0.005\ Å$, $c = 7.865 \pm 0.010\ Å$ and $\beta = 102\,°\ 43' \pm 2'$. Space Group $P2_1/a$—C_{2h}^5. Two centrosymmetric molecules per unit cell. Volume of the unit cell $= 477.8\ Å^3$. Linear absorption coefficient for x-rays $(CuK\alpha)$, $\mu = 9.1$ per cm; total number of electrons per unit cell, 216.

[3] J. M. ROBERTSON, The structure of benzoquinone. Proc. Roy. Soc. [London] A 150 (1935) 106—128.

[4] E. O. WOLLAN, The electron distribution of magnesium oxide. Physic. Rev. 35 (1930) 1019—1027.

[5] B. V. R. MURTY, The space group of anthraquinone. Acta Crystallogr. 8 (1955) 113—114.

[6] B. V. R. MURTY, Atomic form factor curves for carbon and oxygen of $> C = O$ bond of anthraquinone ($25\,°$—$35\,°C$). Acta Crystallogr. 10 (1957) 146—147.

3. Experimental

Determination of integrated intensity was carried out by the photographic method using unfiltered Cu radiation and equi-inclination Weissenberg technique. Relative integrated-intensity measurements were made with Moll recording microphotometer and were put on the absolute scale by comparing with (111) and (200) reflections of aluminium from a powder photograph of a mixture of anthraquinone and aluminium in the ratio 4 to 1 by weight. The intensities of all reflections were corrected for the usual Lorentz and polarization factors and geometrical factor[7]. The $(h0l)$ reflections were corrected for absorption[8] also. Out of a possible number of 1091 different reflections with $CuK\alpha$ radiation, 520 were measured with a high order of accuracy. The weakest and strongest structure factors observed were 1 and 81.6. The observed structure factors are given, along with the corresponding calculated values, in the Table 3.

4. Refinement of the structure

The refinement of the coordinates was made in three steps. All computations were made with Olivetti table-printing calculating machine.

1. Refinement of the X, Z coordinates as far as possible by the application of two successive $(F_o—F_c)$ syntheses for the $(h0l)$ projection since it was very well resolved.

2. Refinement of the Y coordinates by the application of three-dimensional Fourier synthesis for electron density at different points along lines parallel to the Y direction passing through the refined X, Z points of each atom.

3. Final refinement of the X, Y, Z coordinates by the application of three-dimensional differential synthesis.

(a) Difference synthesis

The two-dimensional Fourier projection $(h0l)$ made by SEN[9] was repeated with 134 reflections out of a possible 161 for this projection with the help of BEEVERS and LIPSON strips prepared in this laboratory. To start with, the phases that were given by SEN[1] were adopted. The projection was given in the earlier publication[6]. The R value obtained

[7] G. TUNNEL, The rotation factor for equi-inclination Weissenberg photographs. Amer. Min. **24** (1939) 448—451.

[8] G. ALBRECHT, The absorption factor in crystal spectroscopy. Rev. Sci. Instrum. **10** (1939) 221—222.

[9] S. N. SEN, Electron density map of anthraquinone crystal. Ind. Jour. Physics **19** (1945) 243—246.

was $19^0/_0$ with coordinates derived from this projection and f-curves derived by the author[6] for the different atoms of this substance at laboratory temperature $(25^\circ—35^\circ C)$ at which the experiment was conducted. The above projection was very well resolved and so it was intended to refine the X, Z coordinates of all the atoms by successive two-dimensional $(F_o—F_c)$ syntheses as a first step in the process of refinement. Two successive $(F_o—F_c)$ syntheses were carried out during which the value of R fell to $14.7^0/_0$. Anisotropic f-values were used for oxygen atom in the D_2 synthesis. The D_2 synthesis for $(h0l)$ projection is given in Fig. 1.
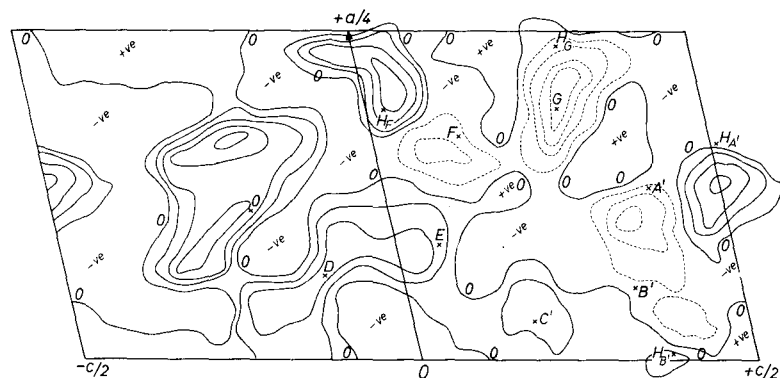

Fig. 1. D_2 synthesis of $(h0l)$ projection. D-values summed up at intervals of $a/60$, $c/30$. Contours are drawn at an interval of $0.2 \, e/\text{Å}^2$. The zero contour is indicated by 0 and negative contours are dotted. Atomic positions after the D_1 synthesis are marked $(\times)$. Contours are drawn surrounding the projected atomic positions. The remaining area of projection is indicated $+ \, ve$ or $— \, ve$.

It can be observed from the D_2 contour diagram that the slope of the D function at B', C' and D was almost nil. The temperature factor chosen for the atom G must have been incorrect as there remains a persistent sharp depression at the position G. The corrected coordinates resulting after the D_2 synthesis were believed to be very close to their real peaks and the further corrections that were to be made to arrive at their final values to be very small. It was considered difficult to arrive at the exact peaks by a further application of D synthesis without a full knowledge of the true anisotropic f curves for all the atoms involved. Instead, at this stage of refinement, an application of differential synthesis[10] was thought worthwhile.

---

[10] A. D. BOOTH, A differential Fourier method for refining atomic parameters in crystal structure analysis. Trans. Faraday Soc. 42 (1946) 444—448.

(b) Three-dimensional Fourier synthesis

So far we have tried to refine only the X, Z coordinates from the $(h0l)$ projection. No attempt was made to refine the Y coordinates. This could not be done from any two-dimensional projection, because the molecular plane is tilted from (010) by $27°$[1], the other tilts being almost negligible. This is how the molecule is quite well resolved in the $(h0l)$ projection and gives rise to too much overlapping in the other projections. So, for the determination of the Y coordinates of the atoms, it was necessary to carry out a three-dimensional Fourier
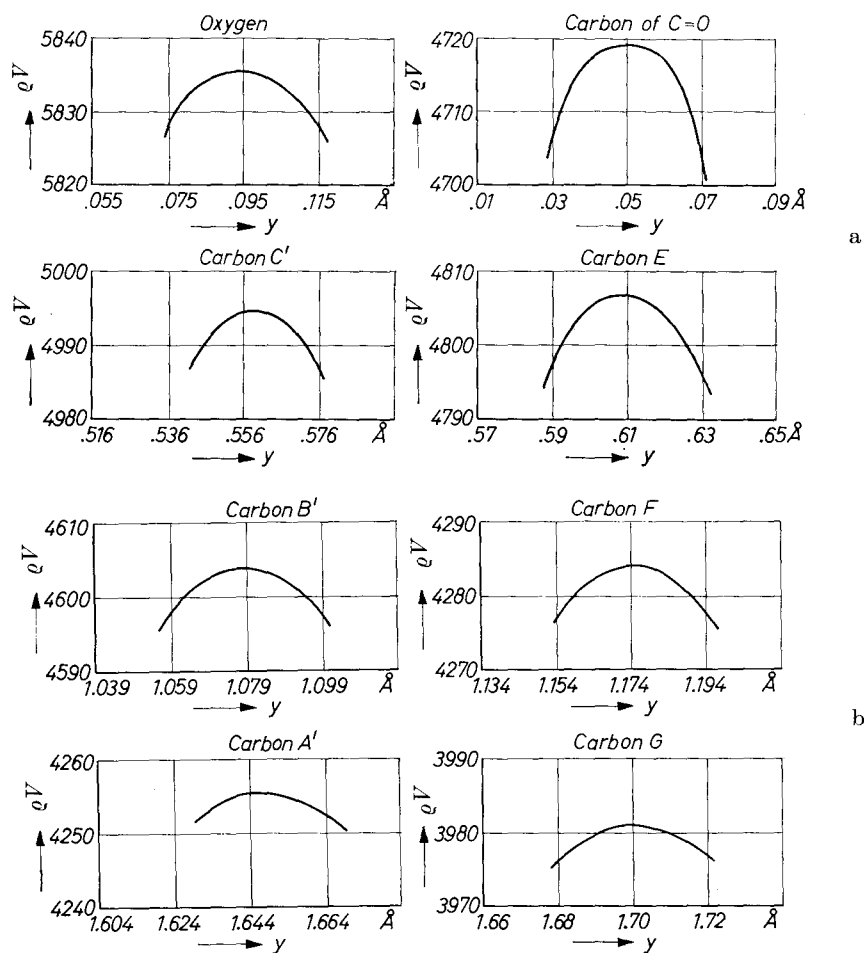

Fig. 2. The variation of (ϱV) with Y for different atoms. Three-dimensional Fourier synthesis.

synthesis at different points along the Y direction through the projected centres of the different atoms in the $(h0l)$ projection obtained after D_2 synthesis. The 520 structure factors mentioned earlier were used in the summation for the electron density. The starting phases for $(hk0)$, $(0kl)$ and (hkl) were calculated with the approximate Y coordinates given by Sen[1]. Electron densities at a few points at intervals of .02 Å on both sides of the expected maximum value along the direction of each atom were computed and the different maxima were located by the method described by Booth[11]. It is interesting to note that the curves of electron density (Fig. 2) plotted against Y for the different atoms of the molecule are more and more diffuse for atoms more and more away from the centre of the molecule, their peak ϱ values being gradually less. This is quite expected because of the possibility of larger amplitudes of thermal vibrations of the end atoms than those of atoms nearer to the centre of the molecule.

c) Differential synthesis

The necessary formulae for the corrections in the X, Y, Z coordinates by the differential synthesis method for monoclinic symmetry were given by Booth[10]. The electron-density distribution of an atom was assumed to possess spherical symmetry at least in the region of its maximum. $\frac{\partial \varrho}{\partial X}$, $\frac{\partial \varrho}{\partial Y}$, $\frac{\partial \varrho}{\partial Z}$ and $\frac{\partial^2 \varrho}{\partial Y^2}$ were obtained by differentiating the Fourier expression for electron density and computed for each atom using all the 520 structure factors. Using these, the corrections in X, Y, Z coordinates of different atoms were calculated. The resulting final coordinates are given in Table 1.

d) Hydrogen atoms

The rough positions of the hydrogen atoms could be located from the D_1 and D_2 syntheses. For better locations of the hydrogen atoms a fresh D_3 synthesis was carried out (excluding the hydrogen atoms) with the final coordinates after differential synthesis of the various carbon and oxygen atoms. Since the final coordinates of the carbon and oxygen atoms are already well refined, if their f curves are correct, hydrogen atoms would be expected to make their appearance in well developed form. The D_3 synthesis is shown in Fig. 3. Hydrogen peak positions from D_3 were located by Booth's method[11]. These gave the tentative X, Z positions of the hydrogen atoms which are verified

[11] A. D. Booth, Fourier technique in organic structure analysis. Cambridge University Press (1948) 63—65.

as described below. The small D values still persistent at the positions of the other atoms were thought to be due to the slight inaccuracies in the f curves.

Approximate Y coordinates of the different hydrogen atoms were calculated by assuming a bond length of 1.0 Å for C—H bond and that the hydrogen atoms also lie in the same molecular plane as the other atoms. This was not unjustified when similar situations were found in naphthalene[12] and anthracene[13]. To test the reality of these hydrogen
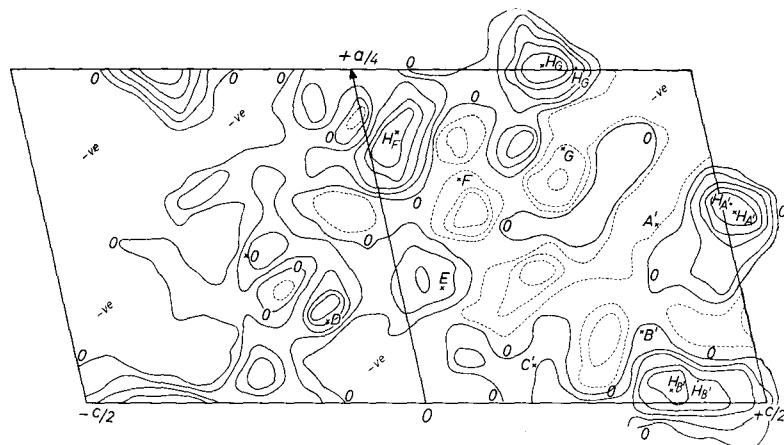

Fig. 3. D_3 synthesis of $(h0l)$ projection. Well developed hydrogen peaks can be observed. Hydrogen peak positions are marked (×). Trial hydrogen positions for H_G, $H_{A'}$ and $H_{B'}$ indicated by dots. Contours are drawn at an interval of 0.2 $e/Å^2$. The zero contours are indicated by 0 and the negative contours are dotted. Other atomic positions after differential synthesis are also marked (×). Contours are drawn surrounding the projected atomic positions. The remaining area of projection is indicated $+ve$ or $-ve$.

positions, the electron density was calculated by using a three-dimensional Fourier synthesis. The electron density for the position H_F indicated in D_3 came out surprisingly well, viz. 1.17 $e/Å^3$. A successive application of differential synthesis for Y of this atom indicated an overall correction of $+$ 0.078 Å. Electron density with the corrected Y was 1.20 $e/Å^3$.

[12] J. M. ROBERTSON, S. C. ABRAHAMS and J. G. WHITE, The crystal and molecular structures of naphthalene. II. Structure investigation by the triple Fourier series method. Acta Crystallogr. 2 (1949) 238—244.

[13] J. M. ROBERTSON, A. M. MATHIESON and V. C. SINCLAIR, The crystal and molecular structure of anthracene, II. Structure investigation by the triple Fourier series method. Acta Crystallogr. 3 (1950) 251—256.

For the H_G and $H_{A'}$ hydrogen atoms attached to the end carbon atoms G and A' of the molecule, the electron densities were calculated to be respectively 0.25 $e/Å^3$ and 0.50 $e/Å^3$ which were not possible at all. A scanning along Y direction in each case did not improve matters. This is apparently due to wrong X, Z coordinates for these atoms. This is an experimental verification of the spuriousness introduced, probably due to f curves of the end atoms influencing the hydrogen positions. A probe into the causes of these low electron densities, obviously wrong X, Z positions, was considered advisable before performing any calculations on the fourth hydrogen atom $H_{B'}$.

A careful study of the X, Z positions of the different hydrogen atoms on the D_3 contour diagram gave a clue to the problem. While the hydrogen H_F ($\varrho = 1.20$ $e/Å^3$) was found to be situated in the D_3 projection almost exactly on the line connecting the opposite carbon atoms of the benzene ring, the positions of the other hydrogen atoms were considerably off for no obvious reason. It was expected that these hydrogen atoms also may be at least close to the symmetrical positions. With this in view and keeping practically the same distances from their respective carbon atoms as in D_3 projection, trials were given by changing the X, Z positions of the hydrogen atoms H_G, $H_{A'}$ and $H_{B'}$. Their new approximate Y coordinates were calculated again by assuming them to be possibly in the molecular plane with a C—H bond of 1.0 Å. Three-dimensional Fourier syntheses for the electron density were carried out at these trial positions. The results immediately appeared as anticipated. The different Y coordinates were then refined by successive application of the differential method again. Electron densities at these positions were calculated to be respectively 0.96, 1.15 and 1.13 $e/Å^3$.

Table 1. *Final coordinates (rounded off to the decimal) of the asymmetric unit of anthraquinone molecule*, molecular centre of symmetry as origin. Coordinates are accurate to within 0.01 Å

Atom	X	Y	Z
A'	2.076 Å	1.646 Å	3.121 Å
B'	0.814 Å	1.080 Å	2.675 Å
C'	0.430 Å	0.560 Å	1.360 Å
E	1.316 Å	0.602 Å	0.490 Å
F	2.609 Å	1.175 Å	0.945 Å
G	3.003 Å	1.702 Å	2.244 Å
D	0.941 Å	0.052 Å	−0.915 Å
O	1.736 Å	0.092 Å	−1.687 Å
H_F	3.188 Å	1.277 Å	0.374 Å
H_G	3.955 Å	2.301 Å	2.565 Å
$H_{A'}$	2.365 Å	2.144 Å	4.030 Å
$H_{B'}$	0.250 Å	1.097 Å	3.219 Å

5. Atomic coordinates, bond lengths, valency angles and molecular plane

The coordinates of the remaining atoms of the unit cell can be readily obtained from the

space-group symmetry $P2_1/a$. The different bond lengths on the basis of the above coordinates were calculated and directly marked in Fig. 4.

The different atoms of the anthraquinone molecule are found to closely conform to a planar configuration. The equation of the molecular plane is given by $-0.3049\,X' + 0.8891\,Y - 0.3414\,Z' = 0$,

where $\qquad\qquad X' = X + Z\cos\beta$

and $\qquad\qquad Z' = Z\sin\beta$,
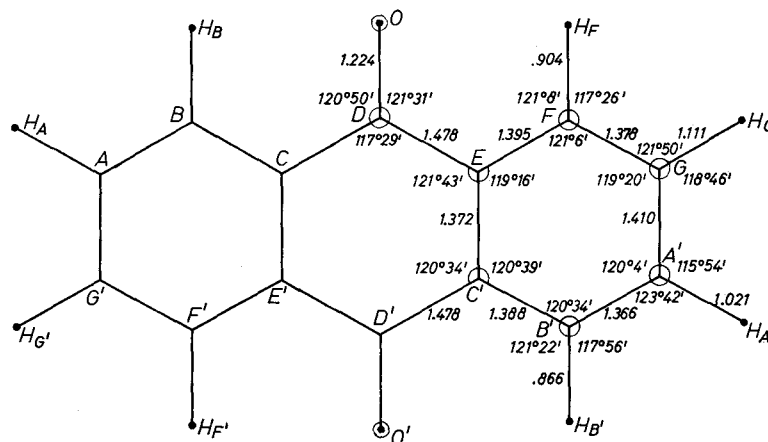
Fig. 4. Bond lengths and bond angles of anthraquinone molecule.

X' Y and Z' being referred to a, b and c^* axes of the unit cell, and -0.3049, $+0.8891$, -0.3414 are the direction cosines of the normal to the plane of the molecule. The different tilts of the normal to the molecular plane with the a, b and c^* axes of the crystal are respectively $107°45'$, $27°14'$, $109°58'$. The tilt of the molecular plane from the plane of $(h0l)$ projection is $27°14'$, as against $27°$ found earlier by SEN[1]. The $> C = O$ bond is tilted from the $(h0l)$ projection by only $2°$, as against $3°48'$ found by SEN. The deviations of the different atoms from the plane indicated above are given in the following table.

Table 2. *Deviation of the atoms from the molecular plane*
$-.3049\,X' + .8891\,Y - .3414\,Z' = 0$

Atom	Deviation	Atom	Deviation
A'	0.001 Å	D	0.002 Å
B'	0.001 Å	O	0.001 Å
C'	0.005 Å	H_F	0.064 Å
E	0.004 Å	H_G	0.158 Å
F	0.002 Å	$H_{A'}$	0.113 Å
G	0.001 Å	$H_{B'}$	0.043 Å

Table 3. *Observed and calculated structure factors*

h k l	F_o	F_c	h k l	F_o	F_c	h k l	F_o	F_c	h k l	F_o	F_c
0 2 0	13.0	15.2	$\overline{20}$ 0 3	3.5	3.6	$\overline{10}$ 0 9	4.0	-2.5	12 3 0	3.6	-4.4
0 0 1	36.7	29.4	2 0 4	43.1	-40.3	$\overline{12}$ 0 9	1.5	-0.2	15 3 0	1.2	-0.2
0 0 2	41.7	-37.2	4 0 4	4.0	-3.4	$\bar{2}$ 0 10	5.3	-4.4	16 3 0	4.3	-2.5
0 0 3	13.1	-10.0	6 0 4	4.0	-4.0	$\bar{4}$ 0 10	8.8	-5.4	1 4 0	1.7	0.5
0 0 4	25.5	-27.7	8 0 4	19.0	18.8	$\bar{8}$ 0 10	4.8	4.5	8 4 0	3.2	-1.6
0 0 5	1.8	-2.8	10 0 4	19.4	24.0	0 1 1	51.5	-57.2	1 1 1	81.6	87.9
0 0 7	6.4	-3.4	12 0 4	3.4	-1.7	0 1 2	8.2	-7.7	2 1 1	29.4	-29.1
0 0 8	2.1	-0.5	$\bar{2}$ 0 4	11.3	7.4	0 1 3	32.9	-27.6	3 1 1	20.6	19.5
2 0 0	38.6	37.4	$\bar{4}$ 0 4	2.5	2.2	0 1 4	11.0	-16.4	4 1 1	2.2	-0.9
4 0 0	42.8	-40.2	$\bar{6}$ 0 4	11.0	-8.8	0 1 5	8.6	11.9	5 1 1	29.6	-31.3
6 0 0	4.8	-6.9	$\bar{8}$ 0 4	10.1	-13.5	0 1 6	1.2	0.3	6 1 1	19.3	-14.3
8 0 0	15.0	-17.5	$\overline{10}$ 0 4	12.0	11.7	0 1 7	3.7	-1.1	7 1 1	15.6	-14.6
10 0 0	4.4	-4.1	$\overline{12}$ 0 4	4.9	5.5	0 2 1	1.6	-1.8	8 1 1	16.0	14.2
12 0 0	5.7	-6.5	$\overline{14}$ 0 4	9.1	-9.6	0 2 2	13.1	-16.5	9 1 1	7.0	-7.8
14 0 0	8.6	-7.2	$\overline{16}$ 0 4	6.8	-5.4	0 2 3	9.0	-12.1	10 1 1	15.8	15.6
16 0 0	4.8	3.3	$\overline{18}$ 0 4	5.3	-3.0	0 2 4	6.7	11.7	13 1 1	4.1	-4.4
2 0 1	8.8	-9.3	2 0 5	10.1	12.3	0 2 5	3.9	6.8	14 1 1	5.5	-5.9
4 0 1	17.3	17.1	4 0 5	6.7	-5.5	0 2 6	5.4	-7.2	15 1 1	4.3	-5.7
6 0 1	52.8	-48.6	6 0 5	4.4	-1.8	0 2 7	2.7	0	$\bar{1}$ 1 1	3.6	-5.4
8 0 1	47.8	-45.3	8 0 5	28.0	27.8	0 2 8	1.5	1.0	$\bar{2}$ 1 1	1.8	-1.7
10 0 1	8.6	7.5	10 0 5	8.5	8.9	0 2 9	1.4	0.4	$\bar{3}$ 1 1	31.7	-25.5
12 0 1	8.8	10.8	12 0 5	5.9	-3.9	0 3 1	1.7	-0.6	$\bar{4}$ 1 1	5.8	-5.8
14 0 1	5.6	-2.2	$\bar{2}$ 0 5	1.8	0.6	0 3 2	4.5	6.0	$\bar{6}$ 1 1	15.8	-12.5
16 0 1	8.3	-7.6	$\bar{4}$ 0 5	11.0	-11.3	0 3 4	4.0	1.1	$\bar{7}$ 1 1	4.9	5.1
$\bar{2}$ 0 1	36.9	41.8	$\bar{6}$ 0 5	4.6	-3.8	0 3 5	4.1	-4.3	$\bar{8}$ 1 1	9.9	12.6
$\bar{4}$ 0 1	24.7	-23.9	$\bar{8}$ 0 5	14.1	17.8	0 3 8	4.8	-5.2	$\bar{9}$ 1 1	6.5	8.4
$\bar{6}$ 0 1	25.8	28.4	$\overline{12}$ 0 5	13.8	-13.4	1 1 0	37.5	34.1	$\overline{11}$ 1 1	6.2	-10.8
$\bar{8}$ 0 1	12.8	16.0	$\overline{14}$ 0 5	7.2	-3.8	2 1 0	63.2	-66.9	$\overline{12}$ 1 1	4.9	5.1
$\overline{12}$ 0 1	16.0	14.7	$\overline{16}$ 0 5	5.2	3.8	3 1 0	41.0	38.1	$\overline{13}$ 1 1	4.4	1.7
$\overline{14}$ 0 1	5.4	0.2	2 0 6	8.1	10.1	4 1 0	19.7	-16.4	$\overline{14}$ 1 1	14.8	12.0
$\overline{18}$ 0 1	3.2	1.8	4 0 6	4.1	-3.2	5 1 0	37.4	-36.5	$\overline{15}$ 1 1	16.4	14.1
$\overline{20}$ 0 1	10.2	-5.2	8 0 6	3.4	-2.0	6 1 0	25.5	-19.9	1 1 2	22.0	-19.9
2 0 2	22.4	20.8	10 0 6	5.3	-3.7	7 1 0	22.3	-17.4	2 1 2	7.3	8.1
4 0 2	14.1	18.1	12 0 6	4.5	2.8	8 1 0	16.9	-15.5	3 1 2	6.6	4.9
6 0 2	10.1	-8.8	$\bar{2}$ 0 6	6.7	3.0	9 1 0	6.7	8.7	5 1 2	22.6	24.5
8 0 2	4.9	-5.8	$\bar{4}$ 0 6	30.4	35.4	10 1 0	5.3	3.4	6 1 2	2.9	1.3
14 0 2	9.1	-7.3	$\bar{6}$ 0 6	14.7	11.7	12 1 0	3.7	-1.9	7 1 2	17.6	-16.1
16 0 2	5.1	-3.7	$\overline{10}$ 0 6	10.0	-6.4	14 1 0	3.8	-1.0	8 1 2	8.1	8.8
18 0 2	2.4	0.4	$\overline{12}$ 0 6	15.7	-16.1	15 1 0	3.8	-6.0	9 1 2	17.4	-19.4
$\bar{2}$ 0 2	32.6	-26.1	$\overline{14}$ 0 6	6.0	-4.3	19 1 0	1.8	3.0	12 1 2	6.3	-7.3
$\bar{4}$ 0 2	26.3	-23.6	$\overline{16}$ 0 6	6.0	3.4	1 2 0	9.1	12.0	16 1 2	4.6	2.5
$\bar{6}$ 0 2	4.4	-2.3	2 0 7	8.6	-6.0	2 2 0	5.3	-5.6	$\bar{1}$ 1 2	9.2	-8.0
$\bar{8}$ 0 2	14.1	-20.7	4 0 7	7.0	-7.2	3 2 0	16.0	-17.4	$\bar{2}$ 1 2	7.0	4.5
$\overline{12}$ 0 2	21.7	21.2	6 0 7	2.8	-0.6	4 2 0	13.4	-18.4	$\bar{3}$ 1 2	7.8	-5.3
$\overline{14}$ 0 2	34.1	36.6	8 0 7	3.0	-2.0	5 2 0	23.9	-25.3	$\bar{5}$ 1 2	20.3	16.3
$\overline{16}$ 0 2	3.5	-0.1	$\bar{2}$ 0 7	7.0	-7.7	6 2 0	10.0	-10.9	$\bar{6}$ 1 2	23.9	-23.2
$\overline{18}$ 0 2	6.1	-4.2	$\bar{4}$ 0 7	21.5	22.4	7 2 0	6.2	8.5	$\bar{7}$ 1 2	18.8	-15.8
$\overline{20}$ 0 2	3.1	-3.1	$\bar{6}$ 0 7	25.4	26.3	8 2 0	6.3	9.6	$\bar{8}$ 1 2	8.8	-8.8
2 0 3	51.9	-50.4	$\bar{8}$ 0 7	4.9	-6.3	10 2 0	6.2	10.5	$\bar{9}$ 1 2	8.4	-9.0
6 0 3	20.5	22.8	$\overline{10}$ 0 7	7.0	-4.1	11 2 0	2.6	-2.4	$\overline{10}$ 1 2	9.0	-9.9
8 0 3	6.7	-4.7	$\overline{14}$ 0 7	2.8	0.7	12 2 0	6.1	-7.0	$\overline{11}$ 1 2	15.6	14.0
10 0 3	4.4	-5.4	$\overline{16}$ 0 7	2.8	1.3	13 2 0	7.5	-5.4	$\overline{12}$ 1 2	20.9	-17.6
12 0 3	2.5	-3.8	2 0 8	9.0	-8.6	14 2 0	1.8	-1.9	$\overline{13}$ 1 2	10.0	6.6
14 0 3	4.7	-1.0	6 0 8	4.9	3.7	15 2 0	6.7	-3.9	$\overline{14}$ 1 2	6.0	5.6
16 0 3	4.8	3.4	$\bar{2}$ 0 8	5.4	5.3	16 2 0	7.1	4.2	$\overline{15}$ 1 2	10.4	9.2
$\bar{2}$ 0 3	29.0	29.6	$\bar{4}$ 0 8	3.7	-4.0	1 3 0	0.9	6.9	$\overline{16}$ 1 2	10.9	9.2
$\bar{4}$ 0 3	12.5	14.4	$\bar{6}$ 0 8	3.0	-0.2	2 3 0	9.3	-11.0	1 1 3	36.2	-36.4
$\bar{6}$ 0 3	53.3	-50.8	$\bar{8}$ 0 8	6.6	-3.7	3 3 0	5.9	-8.0	2 1 3	9.7	-7.9
$\bar{8}$ 0 3	23.8	-23.2	$\overline{12}$ 0 8	6.6	5.7	4 3 0	1.7	2.6	4 1 3	6.1	6.0
$\overline{10}$ 0 3	7.0	6.9	$\overline{14}$ 0 8	1.2	-0.2	5 3 0	1.6	-6.9	7 1 3	7.4	11.1
$\overline{12}$ 0 3	7.2	1.7	2 0 9	2.6	1.2	6 3 0	2.2	5.4	8 1 3	5.2	5.3
$\overline{14}$ 0 3	15.4	13.1	$\bar{2}$ 0 9	3.0	1.0	8 3 0	2.5	5.0	9 1 3	8.1	7.9
$\overline{16}$ 0 3	3.4	4.3	$\bar{4}$ 0 9	3.1	-2.0	9 3 0	5.8	-1.9	10 1 3	3.8	4.7
$\overline{18}$ 0 3	6.4	-3.5	$\bar{6}$ 0 9	4.9	-3.8	10 3 0	1.7	-4.5	11 1 3	3.9	-5.8
			$\bar{8}$ 0 9	3.8	-1.1	11 3 0	2.8	-2.8	14 1 3	5.3	3.5

Table 3. (continued)

h k l	F_o	F_c	h k l	F_o	F_c	h k l	F_o	F_c	h k l	F_o	F_c
$\bar{1}$ 1 3	24.6	− 21.2	$\bar{4}$ 1 7	16.4	− 14.6	$\bar{2}$ 2 3	20.8	− 19.5	2 3 1	6.6	8.3
$\bar{4}$ 1 3	31.8	28.5	$\bar{5}$ 1 7	7.1	5.6	$\bar{3}$ 2 3	5.7	− 8.9	3 3 1	3.7	6.2
$\bar{5}$ 1 3	3.3	− 1.6	$\bar{8}$ 1 7	6.1	6.9	$\bar{4}$ 2 3	2.1	6.1	4 3 1	9.0	− 11.2
$\bar{6}$ 1 3	6.6	7.4	$\bar{9}$ 1 7	3.6	− 2.8	$\bar{5}$ 2 3	2.3	− 2.1	5 3 1	9.3	6.8
$\bar{7}$ 1 3	11.9	− 9.3	$\bar{11}$ 1 7	6.1	− 5.3	$\bar{7}$ 2 3	3.1	4.8	6 3 1	11.5	− 11.9
$\bar{8}$ 1 3	10.8	− 10.9	$\bar{12}$ 1 7	4.1	3.7	$\bar{9}$ 2 3	7.7	− 8.9	$\bar{1}$ 3 1	6.1	− 8.1
$\bar{9}$ 1 3	20.5	− 20.9	4 1 8	4.0	3.2	$\bar{10}$ 2 3	14.0	13.8	$\bar{3}$ 3 1	14.0	− 20.5
$\bar{10}$ 1 3	4.1	− 2.6	$\bar{3}$ 1 8	5.9	6.8	$\bar{11}$ 2 3	17.2	− 17.5	$\bar{4}$ 3 1	10.1	8.9
$\bar{11}$ 1 3	14.3	14.0	$\bar{4}$ 1 8	4.2	− 4.8	$\bar{12}$ 2 3	7.8	10.3	$\bar{5}$ 3 1	4.6	− 3.5
$\bar{12}$ 1 3	13.7	− 11.9	$\bar{5}$ 1 8	4.9	4.6	$\bar{16}$ 2 3	3.4	− 2.8	$\bar{7}$ 3 1	4.3	7.2
$\bar{13}$ 1 3	24.8	21.6	$\bar{6}$ 1 8	4.4	− 3.8	1 2 4	3.4	− 4.9	$\bar{8}$ 3 1	4.9	− 1.7
$\bar{14}$ 1 3	9.0	− 9.9	$\bar{7}$ 1 8	5.0	− 5.6	2 2 4	3.2	− 6.3	$\bar{9}$ 3 1	6.3	− 2.0
1 1 4	3.5	− 2.2	$\bar{10}$ 1 8	5.1	− 3.6	4 2 4	3.9	1.1	$\bar{10}$ 3 1	6.7	− 4.7
2 1 4	17.4	15.0	1 2 1	9.0	− 5.9	5 2 4	19.5	21.0	$\bar{11}$ 3 1	8.8	− 7.9
3 1 4	30.4	− 27.8	2 2 1	31.6	42.6	6 2 4	7.6	9.8	2 3 2	6.3	− 4.6
4 1 4	8.4	8.7	3 2 1	44.6	− 46.3	7 2 4	5.7	4.3	3 3 2	17.2	19.3
6 1 4	11.7	11.0	4 2 1	26.3	33.2	9 2 4	5.7	− 6.1	4 3 2	15.6	− 15.4
7 1 4	32.8	29.0	5 2 1	6.2	− 8.5	12 2 4	2.9	− 4.0	5 3 2	20.2	24.5
8 1 4	21.7	18.3	6 2 1	7.0	− 11.2	$\bar{1}$ 2 4	6.9	5.1	6 3 2	7.0	5.7
9 1 4	7.3	10.0	7 2 1	2.6	4.2	$\bar{2}$ 2 4	3.1	− 1.6	12 3 2	5.5	3.5
12 1 4	5.7	− 7.6	10 2 1	3.4	− 1.5	$\bar{3}$ 2 4	9.9	12.2	$\bar{1}$ 3 2	6.1	− 9.4
$\bar{1}$ 1 4	2.6	5.0	12 2 1	8.3	− 4.6	$\bar{4}$ 2 4	8.8	− 12.4	$\bar{2}$ 3 2	11.5	− 13.3
$\bar{2}$ 1 4	15.1	− 16.1	$\bar{1}$ 2 1	11.4	14.6	$\bar{5}$ 2 4	7.4	8.8	$\bar{3}$ 3 2	12.4	− 12.1
$\bar{3}$ 1 4	3.3	− 4.9	$\bar{2}$ 2 1	10.0	− 11.2	$\bar{10}$ 2 4	7.5	8.7	$\bar{4}$ 3 2	5.0	− 5.7
$\bar{4}$ 1 4	6.2	5.9	$\bar{3}$ 2 1	4.9	− 4.7	$\bar{11}$ 2 4	5.0	− 4.0	$\bar{5}$ 3 2	6.0	− 1.4
$\bar{5}$ 1 4	31.6	− 27.2	$\bar{4}$ 2 1	13.3	− 18.4	$\bar{12}$ 2 4	8.6	10.8	$\bar{7}$ 3 2	4.0	3.1
$\bar{6}$ 1 4	9.5	9.5	$\bar{5}$ 2 1	5.3	7.5	$\bar{14}$ 2 4	7.6	− 5.2	2 3 3	4.8	− 2.9
$\bar{7}$ 1 4	11.1	− 10.6	$\bar{6}$ 2 1	12.9	− 13.1	$\bar{16}$ 2 4	4.5	− 3.2	3 3 3	13.8	10.8
$\bar{9}$ 1 4	10.3	13.2	$\bar{7}$ 2 1	5.5	− 2.8	2 2 5	5.4	− 3.2	4 3 3	16.7	16.6
$\bar{15}$ 1 4	4.9	− 3.1	$\bar{8}$ 2 1	6.4	− 6.5	3 2 5	7.0	4.0	5 3 3	12.4	14.2
2 1 5	8.3	9.6	$\bar{9}$ 2 1	5.5	− 1.6	4 2 5	7.9	− 11.7	6 3 3	9.2	7.5
3 1 5	7.6	− 9.9	$\bar{10}$ 2 1	3.4	− 4.0	5 2 5	3.2	4.8	8 3 3	4.8	− 5.8
5 1 5	3.3	0.3	$\bar{11}$ 2 1	4.4	3.7	6 2 5	6.3	− 8.4	11 3 3	5.0	− 5.5
6 1 5	8.0	9.1	$\bar{12}$ 2 1	2.7	− 4.3	7 2 5	3.6	− 3.1	$\bar{4}$ 3 3	6.5	− 4.7
9 1 5	5.3	6.0	$\bar{15}$ 2 1	7.1	3.6	9 2 5	3.0	2.7	$\bar{7}$ 3 3	4.7	1.4
10 1 5	11.8	− 11.0	$\bar{16}$ 2 1	9.4	7.8	11 2 5	3.8	− 2.2	$\bar{8}$ 3 3	13.4	− 10.0
11 1 5	10.5	9.5	1 2 2	20.7	− 24.1	$\bar{4}$ 2 5	8.9	− 11.7	$\bar{9}$ 3 3	7.7	2.2
12 1 5	9.8	− 2.9	2 2 2	25.9	31.7	$\bar{5}$ 2 5	7.5	8.0	1 3 4	3.9	− 4.0
$\bar{4}$ 1 5	8.0	10.5	3 2 2	3.0	− 3.7	$\bar{6}$ 2 5	8.2	9.8	$\bar{1}$ 3 4	5.9	− 1.0
$\bar{5}$ 1 5	7.3	10.7	4 2 2	3.7	7.8	$\bar{7}$ 2 5	11.5	12.4	$\bar{2}$ 3 4	9.6	7.6
$\bar{6}$ 1 5	5.7	2.8	5 2 2	2.1	1.4	$\bar{8}$ 2 5	11.4	15.1	$\bar{6}$ 3 4	6.3	4.8
$\bar{7}$ 1 5	4.7	2.0	6 2 2	2.3	− 2.1	$\bar{9}$ 2 5	3.0	1.6	$\bar{7}$ 3 4	9.5	3.3
$\bar{9}$ 1 5	5.1	5.7	9 2 2	10.4	7.2	$\bar{12}$ 2 5	4.7	− 5.5	$\bar{9}$ 3 4	18.8	14.3
$\bar{13}$ 1 5	12.9	− 11.4	10 2 2	11.0	− 12.9	$\bar{14}$ 2 5	7.5	− 5.1	$\bar{10}$ 3 4	10.8	− 9.7
$\bar{14}$ 1 5	5.4	− 4.5	11 2 2	5.6	6.2	1 2 6	3.2	− 4.4	$\bar{11}$ 3 4	7.4	6.2
$\bar{15}$ 1 5	5.9	− 4.1	14 2 2	2.7	3.7	2 2 6	3.5	− 1.5	5 3 5	6.0	− 5.6
2 1 6	3.6	− 4.8	$\bar{1}$ 2 2	15.2	− 15.5	$\bar{2}$ 2 6	4.6	− 6.7	6 3 5	5.8	4.0
4 1 6	3.9	− 6.4	$\bar{2}$ 2 2	18.7	− 20.3	$\bar{5}$ 2 6	4.5	− 6.9	$\bar{1}$ 3 5	7.7	− 4.8
8 1 6	6.7	− 4.4	$\bar{3}$ 2 2	5.2	− 7.5	$\bar{6}$ 2 6	4.3	5.2	$\bar{2}$ 3 5	4.4	5.4
9 1 6	6.6	4.2	$\bar{4}$ 2 2	13.8	18.0	$\bar{7}$ 2 6	7.3	7.6	$\bar{3}$ 3 5	7.4	− 7.6
$\bar{2}$ 1 6	9.3	− 9.9	$\bar{5}$ 2 2	6.2	3.5	$\bar{8}$ 2 6	7.4	9.4	$\bar{8}$ 3 5	10.2	7.2
$\bar{4}$ 1 6	3.8	4.6	$\bar{6}$ 2 2	6.8	11.0	$\bar{9}$ 2 6	9.1	11.4	$\bar{9}$ 3 5	14.1	10.0
$\bar{5}$ 1 6	17.1	15.7	$\bar{8}$ 2 2	3.9	− 3.9	$\bar{12}$ 2 6	3.0	− 3.0	$\bar{10}$ 3 5	7.7	5.7
$\bar{6}$ 1 6	21.0	18.5	$\bar{9}$ 2 2	11.6	− 16.3	4 2 7	2.7	4.1	$\bar{11}$ 3 5	6.5	3.7
$\bar{7}$ 1 6	26.9	23.2	$\bar{10}$ 2 2	7.3	− 10.2	6 2 7	2.3	− 0.6	4 3 6	4.0	1.6
$\bar{8}$ 1 6	6.5	5.0	$\bar{11}$ 2 2	3.6	− 2.3	$\bar{1}$ 2 7	9.8	− 10.5	5 3 6	5.4	− 3.8
$\bar{9}$ 1 6	4.3	− 6.0	1 2 3	3.2	4.5	$\bar{2}$ 2 7	2.8	1.2	$\bar{1}$ 3 6	4.1	− 4.3
$\bar{10}$ 1 6	3.5	3.9	2 2 3	7.7	− 13.5	$\bar{8}$ 2 7	6.2	− 6.1	$\bar{2}$ 3 6	6.3	− 4.5
$\bar{11}$ 1 6	11.1	− 10.9	5 2 3	7.2	7.1	$\bar{9}$ 2 7	3.9	3.6	$\bar{3}$ 3 6	4.4	− 3.8
$\bar{13}$ 1 6	4.0	− 2.7	6 2 3	21.1	28.9	$\bar{10}$ 2 7	5.9	− 5.7	$\bar{1}$ 3 8	4.2	3.9
$\bar{14}$ 1 6	4.8	− 4.0	7 2 3	17.2	16.0	$\bar{12}$ 2 7	2.2	− 1.1	$\bar{7}$ 3 8	4.1	− 4.8
1 1 7	8.2	− 10.4	8 2 3	4.5	7.2	$\bar{1}$ 2 8	3.0	− 3.2	4 4 2	9.9	11.6
2 1 7	4.2	− 4.8	9 2 3	2.9	2.6	$\bar{2}$ 2 8	8.4	9.0	2 4 3	6.4	2.3
$\bar{2}$ 1 7	8.7	− 9.1	10 2 3	6.9	− 7.8	$\bar{3}$ 2 8	6.5	− 5.8	4 4 3	7.2	6.0
$\bar{3}$ 1 7	17.8	16.9	$\bar{1}$ 2 3	6.2	− 7.6	$\bar{4}$ 2 8	3.4	2.7	5 4 3	8.3	− 6.1

6. Observed and calculated structure factors

On the basis of the final refined coordinates of the different atoms of the asymmetric unit given in Table 1 and the f curves mentioned earlier, a set of structure factors for all the 520 reflections measured was calculated. Anisotropic f values of oxygen were used for ($h0l$) reflections. The observed and calculated structure factors are given in Table 3.

7. Data concerning the different atoms of anthraquinone

As described before, the exact positions of the different atoms of anthraquinone were fixed up by the use of the differential synthesis method. Electron densities at these positions were calculated by the three-dimensional Fourier synthesis, and a further attempt was made to make out the shapes of the different atoms. For this purpose the X, Z positions of the different atoms were kept fixed and electron densities were calculated in the positive direction of Y at the distances of 0.1, 0.2, 0.3, 0.5, 0.7, and 1.0 Å from the centre of each atom. The electron density was plotted as ordinates against distance from the centre of the atoms in the Y direction as abscissae for each atom, and the curves for different atoms are given in Fig. 5. The shapes of these different atoms up to a distance of 0.5 Å from the centre of the atom may be closely approximated by the well known form[14,15]

$$\varrho_r = \varrho_0\, e^{-pr^2}$$

where ϱ_r is the electron density at a distance of r from the centre of the atom, ϱ_0 is the electron density at $r = 0$ and p, a constant, different for different atoms. No attempt to find the total electron count for an atom from the electron-density curve was made since it would be necessary to draw the electron-density curve for an atom in different directions to include the influence of different bonds. Instead, a total electron count for each atom had already been carried out while estimating the form-factor curves[6]. The peak electron density ϱ_0, p, curvatures and the total electron count for the different atoms are given in Table 4.

[14] W. Costain, Ph. D. Thesis, University of Birmingham (1941).

[15] A. D. Booth, The accuracy of atomic coordinates derived from Fourier series in x-ray structure analysis. Proc. Roy. Soc. [London] A 188 (1946) 77—92.
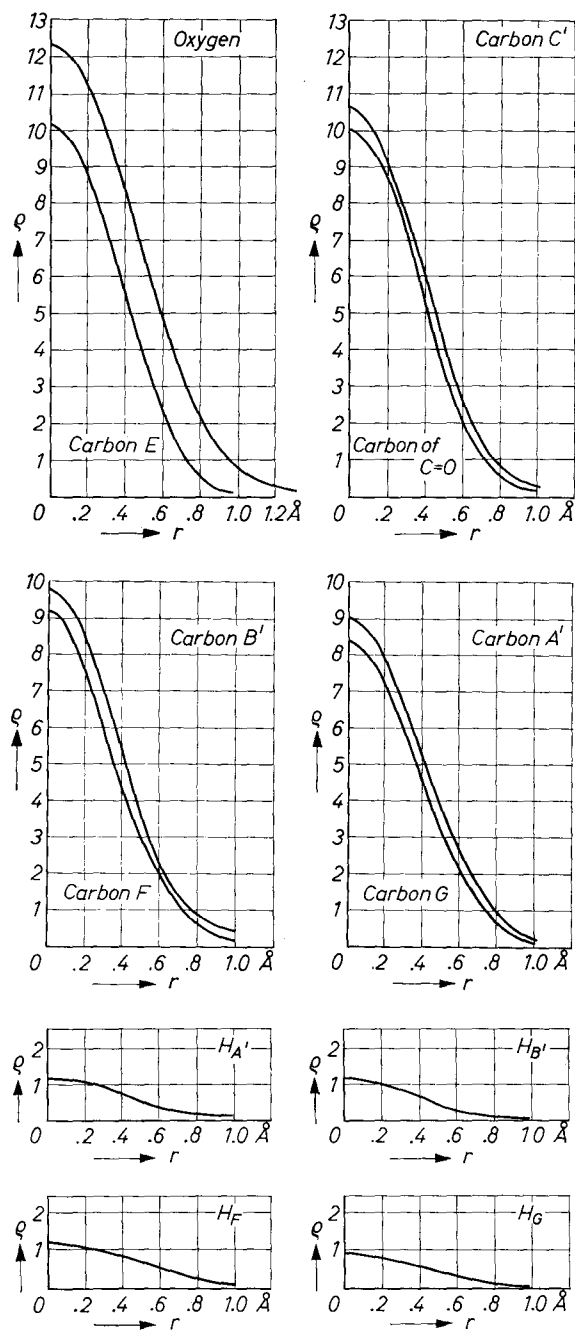
Fig. 5. Shapes of different atoms: variation of ϱ with r along the Y direction.

Table 4. *Data concerning the different atoms of anthraquinone*

Atom	Peak electron density $e/\text{Å}^3$	p	Curvature	Total electron count
A'	8.95	4.10	—53.04	5.98
B'	9.68	4.32	—65.87	6.00
C'	10.51	4.56	—75.33	5.96
E	10.04	4.43	—71.73	5.96
F	9.07	4.14	—59.84	6.00
G	8.37	3.92	—52.83	5.97
D	9.93	4.96	—68.78	4.98
O	12.29	3.87	—58.46	8.97
H_F	1.21		— 7.93	
H_G	0.96		—10.64	
$H_{A'}$	1.16		— 4.22	
$H_{B'}$	1.14		— 6.66	

8. Accuracy of the structure

As was already mentioned, BOOTH's[16] R test for the $(h0l)$ projection was taken as a general guide during the preliminary stages of refinement of the structure. The final R value for all observed reflections was calculated using the F_o and F_c values given in the Table 3. The different R values for the different projections, along with the general R value including all reflections are given in Table 5.

Table 5. *Comparison of R values*

Projection or group	Number of different reflections observed	R
$(h0l)$	134	15.1%
$(hk0)$	44	18.6
$(0kl)$	21	20.6
general, including all the reflections observed	520	19.6
Reflections with $F > 10$	153	12.2
Reflections with $\sin\theta < 0.6$	202	15.7

The causes of the persistent high value of R may be possibly due to
(i) random errors in the measured structure factors,
(ii) errors in the f curves,

[16] A. D. BOOTH, An expression for following the process of refinement in x-ray structure analysis using Fourier series. Phil. Mag. **36** (1945) 609—615.

(iii) likely increase in intensities of weak reflections due to Renninger reflections[17], of which this crystal forms a good example[5].

Out of the 520 reflections observed, the number of reflections having structure factors greater than 10 is only 153, the remaining 367 having structure factors less than 10. There is a greater possibility of committing a larger percentage error in the measurement of weak reflections than in the medium and the intense ones. This is indicated by the fall in the R value to 12.2% for reflections with $F_o > 10$.

It may be recalled that in calculating the F_c values the f curves of all the carbon atoms were assumed to be spherically symmetrical. Only for $(h0l)$ reflections anisotropic f values of oxygen were used. For all the other reflections a mean of the f curves along the major and minor axes of oxygen was used. For hydrogen atoms Hartree f curves (International tables for the determination of crystal structure, p. 571) was used. All these put together might have led to slightly incorrect F_c values which would have been reflected in the R values. This also might be due to the f curves being slightly incorrect at higher angles as is indicated by the R value again falling down to 15.7% when the reflections with $\sin \theta > 0.6$ are omitted.

Finally mention must be made about the contribution of the Renninger effect to the R value. It might just be possible that some sets of strong reflections are giving rise to the Renninger reflections in the direction of some weaker reflections thereby appreciably increasing their measured intensities (Banerjee[18]). A few of these occuring at the absent-spectra positions $(h0l)$ with h odd[5] are even of measurable intensity and are of intensity quite higher than that of the weakest reflection measured.

Following the above discussion on the R value it can be well understood that it cannot serve for a quantitative estimation of the accuracy of the structure obtained by a high degree of refinement. A more reasonable approach to the problem is to calculate the standard deviation in the various results that were obtained.

Comparison of independent measurements of structure factors by the present author and Sen[1] indicated a mean deviation of 10% in the medium and intense structure factors and a constant mean deviation of about 1 in the weak values. The formulae for standard deviation of

[17] M. Renninger, Röntgenometrische Beiträge zur Kenntnis der Ladungsverteilung im Diamantgitter. Z. Kristallogr. 97 (1937) 107—121.

[18] K. Banerjee, Small Fourier terms in crystal structure analysis and Renninger effect. Proc. Nat. Acad. Sci. Ind. 23 (1955), Parts IV and V, 39.

electron density, $\sigma(\varrho)$, and standard deviation in the coordinates $\sigma(X)$ due to a deviation in the measured structure factors were given by LIPSON and COCHRAN[19]. Using the value of $\sigma(F_o)$ as stated above for anthraquinone, the standard deviation in the electron density and coordinates were calculated seperately on the two assumptions and the results are given in Table 6.

Table 6. *Standard deviation in electron density and atomic coordinates due to random errors in the measurement of F_o*

Atom	Assuming $\sigma(F_o) = 1$		Assuming $\sigma(F_o) = .1\ (F_o)$	
	$\sigma(\varrho_0)\,e/\text{Å}^3$	$\sigma(X_n)\,\text{Å}$	$\sigma(\varrho_0)\,e/\text{Å}^3$	$\sigma(X_n)\,\text{Å}$
A'	0.14	0.0060	0.12	0.0059
B'	0.14	0.0058	0.13	0.0055
C'	0.14	0.0050	0.13	0.0051
E	0.14	0.0054	0.13	0.0054
F	0.14	0.0064	0.12	0.0058
G	0.14	0.0073	0.12	0.0062
D	0.14	0.0049	0.17	0.0057
O	0.14	0.0053	0.12	0.0042

Table 7. *Standard deviation in electron density*, $\sigma(\varrho_0) = .22\ e/\text{Å}^3$. *Standard deviations in coordinates*

Atom	$\sigma(X)$ Å	$\sigma(Y)$ Å	$\sigma(Z)$ Å	$\sigma(\text{R.M.S.})$ Å	Mean $\sigma(\text{R.M.S.})$Å
A'	0.0115	0.0124	0.0105	0.0115	
B'	0.0093	0.0100	0.0084	0.0093	
C'	0.0081	0.0087	0.0074	0.0081	
E	0.0085	0.0092	0.0077	0.0085	0.0098
F	0.0102	0.0110	0.0093	0.0102	
G	0.0116	0.0124	0.0105	0.0115	
D	0.0089	0.0096	0.0081	0.0089	
O	0.0105	0.0112	0.0095	0.0104	
H_F	0.0771	0.0829	0.0699	0.0768	
H_G	0.0575	0.0618	0.0521	0.0573	0.0925
$H_{A'}$	0.1449	0.1557	0.1314	0.1443	
$H_{B'}$	0.0918	0.0987	0.0833	0.0915	

[19] H. LIPSON and W. COCHRAN, The determination of crystal structure· Crystalline State Vol. III. Bell, London (1953) 288.

[20] D. W. J. CRUICKSHANK, The accuracy of electron density maps in x-ray analysis with special reference to dibenzyl. Acta Crystallogr. 2 (1949) 65—82.

Using the expressions derived by CRUICKSHANK[20] the standard deviation in electron density and coordinates based on the measured structure factors and calculated structure factors given in the Table 3 are calculated and given in Table 7.

Standard deviations in the different bond lengths in the asymmetric unit were calculated using the relation $\sigma^2_{AB} = \sigma^2_A + \sigma^2_B$ where σ_{AB} denotes standard deviation in the bond length between two atoms A and B and the results are given in Table 8.

Table 8. *Standard deviation in bond lengths*

Bond		Bond length Å	Standard deviation Å
$A'B'$	(C—C)	1.366	0.0148
$B'C'$	(C—C)	1.388	0.0123
$C'E$	(C—C)	1.372	0.0117
EF	(C—C)	1:395	0.0133
FG	(C—C)	1.378	0.0154
GA'	(C—C)	1.410	0.0163
ED	(C—C) single	1.478	0.0122
$C'D'$	(C—C) single	1.478	0.0120
DO	(C=O)	1.224	0.0137
FH_F	(C—H)	0.904	0.0775
GH_G	(C—H)	1.111	0.0584
$A'H_{A'}$	(C—H)	1.021	0.1448
$B'H_{B'}$	(C—H)	0.866	0.0920

The above values of the standard deviation in bond lengths corresponds to a standard deviation of the order of $1°$ for the bond angles.

9. Discussion of results

The anthraquinone molecule with all its carbon and oxygen atoms forms a planar structure with a maximum deviation 0.005 Å for the carbon C'. In view of the mean R.M.S. standard deviation 0.0098 Å of the carbon and oxygen atoms, this deviation may very well be imagined to be due to the series-termination effect. Even the hydrogen atoms are found to be in the molecular plane within the limits of mean R.M.S. standard deviation 0.0925 Å obtained for them separately. Under these considerations the planar structure of the anthraquinone molecule is highly probable. Similar conclusions were arrived at for the aromatic hydrocarbons naphthalene and anthracene[12,13].

Refering to the molecular picture in space given in Fig. 4, the bond lengths of the chemically equivalent bonds are only slightly different as shown in Table 9. Analysis of these differences by applying the numerical levels of significance tests[20], shows them in high probability to be by chance, so we are justified in averaging these chemically equivalent bonds and the modified picture of the molecule in space
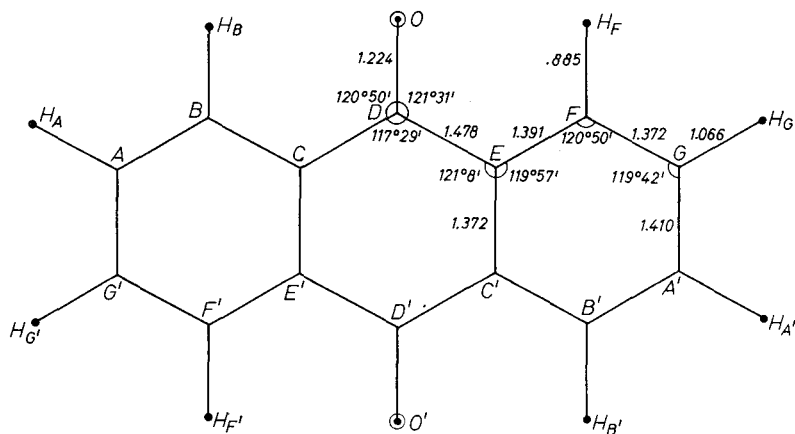

Fig. 6. Molecular diagram. Chemically equal bonds are averaged

becomes as shown in Fig. 6. The difference between the chemically different C—C bonds of the end benzene rings in the anthraquinone molecule are not by chance and are significant as shown in Table 9.

Table 9. *Significance tests*

	Bonds	Difference δl	Mean standard deviation of the bond σ	$\dfrac{\delta l}{\sigma}$	Probability of difference being by chance P
Chemically equivalent	DE and $D'C'$	0.000			
	EF and $C'B'$	0.007	0.0128	0.5469	well above 5%
	FG and $B'A'$	0.012	0.0151	0.7984	well above 5%
Chemically different	FG and $A'G$	0.032	0.0159	2.012	1% to 5%
	EF and EC'	0.023	0.0125	1.840	1% to 5%
	EC' and GA'	0.038	0.0140	2.714	0.1% to 1%

For anthraquinone, four stable valence bond structures can be formulated (Fig. 7). By superposing and averaging these possible

resonance structures, each of the bonds in the outer benzene rings possesses a double bond character of 50% and the interatomic distance corresponding to Pauling and Brockway curve[21] is 1.39 Å.

The differences thus seen between this approximate method of treatment and the present analysis of the structure may become explicable when the much more numerous excited structures for anthraquinone are considered. The C—C single bond (DE) in the central benzene ring of the molecule is 1.478 Å with a mean standard deviation of 0.0121 Å, and is only slightly less than the C—C single bond observed
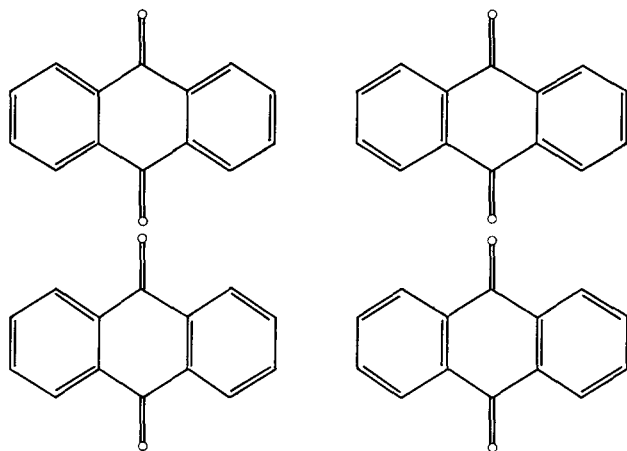
Fig. 7. Canonical structures of anthraquinone

in other aromatic compounds. In view of the partial ionization of the $> C = O$ bond[6] this slight decrease in the length of the C—C single bond may be quite plausible. According to the idea given by Pauling[22], the effect of formal positive charge on an atom is to reduce its covalent radius, and the effect of the formal negative charge is to give an opposite effect. In the DE bond, D is positively charged and so a slight reduction in its radius is expected, resulting in the shortening of the bond. It is difficult to make any quantitative estimation unless the effect of partial ionization of a particular bond on the neighbouring atoms is better understood. Finally coming to the $> C = O$ bond $(DO$ in Fig. 6) it is interesting to note that it is much longer (1.224 Å)

[21] L. Pauling and L. O. Brockway, Carbon-carbon bond distances. Revised values of covalent radii. J. Amer. Chem. Soc. 59 (1937) 1223—1236.

[22] L. Pauling, The nature of chemical bond. Oxford University Press (1939) 75.

than what it was previously observed (1.15 Å) . The standard deviation
of this bond being only 0.0137 Å, the difference becomes quite signifi-
cant. This increase from the previously observed value is not surprising
if we consider the ionic character of the bond. Following the reasoning
by Pauling[22] and Lowry[23] 'for multiple bonds between atoms of
different electronegativity such as the carbon-oxygen double bond in
aldehydes and ketones', it is expected that in the anthraquinone

$> C = O$ bond a resonance between $> C :: \ddot{O}:$ and $> C^+ : \ddot{O}:^-$ is more
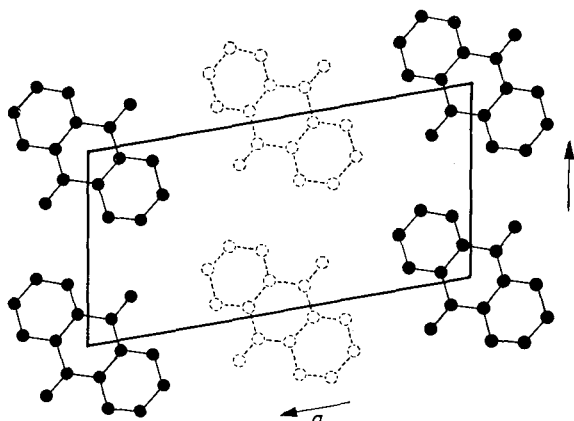
Fig. 8. Projection on (010). The dotted molecules have their centres in planes $b/2$
above and below the black ones

likely. The observed bond length for this bond is in close agreement
with that obtained by Pauling for this bond (1.24 Å). The bond length
of $> C = O$ observed in 1,5 dichloroanthraquinone[24] is 1.25 Å.

More or less good symmetry is displayed in the C—H bonds. The
bonds with carbon atoms (B' and F) nearer to the centre of the molecule
are very nearly equal to one another. The bonds attached to the end
carbon atoms (A' and G) are roughly equal to each other, but differ
slightly from the other group. The C—H bond observed in anthracene[13]
is 1.10 Å and those observed in adenine hydrochloride[25] are 1.00 Å
and 0.85 Å. The average value of the chemically equivalent C—H bonds

[23] T. M. Lowry, Studies of electrovalency, Part I—The polarity of double
bonds. J. Chem. Soc. 123 (1923) 822—831.

[24] M. Bailey, The crystal structure of 1:5—dichloroanthraquinone. Acta
Crystallogr. 11 (1958) 103—107.

[25] W. Cochran, The structures of pyrimidines and purines. Acta Crystallogr.
4 (1951) 81—92.

in anthraquinone are 0.885 Å and 1.066 Å with a mean standard deviations of 0.085 and 0.102. These values agree well within experimental error with the values observed in other crystals and the expected value of 1.08 Å for the bond[22].

The peak densities of the atoms fall gradually on passing from the centre of the molecule outwards (Table 4), with greater spread in the electron distribution for the end atoms. This effect, also observed in naphthalene and anthracene, is readily explicable if we adopt the idea of ROBERTSON et al.[12,13], that the molecule is supposed to be a rigid body vibrating about its centre.

The arrangement of molecules in the anthraquinone crystal can be well understood from its b axis projection (Fig. 8). Molecules are grouped in a zigzag way in space with their planes in consecutive layers being inclined to one another at an angle of 54° 28'. Molecules are, however, very well resolved in the (010) plane. The molecular nearest approach is 3.51 Å.

Acknowledgements