

The Crystal and Molecular Structure of 9:10-Anthrahydroquinone Dibenzoate

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The structure of 9:10-anthrahydroquinone dibenzoate was determined by the application of two- and three-dimensional transforms together with Fourier projections. The atomic coordinates and asymmetric temperature factors were refined by the least-squares method. The crystals are triclinic with one molecule per unit cell:

$$a = 8.91, b = 12.60, c = 5.83 \text{ \AA}; \alpha = 105.2^\circ, \beta = 106.5^\circ, \gamma = 58.2^\circ.$$

Space group $P\bar{1}$. For the three axial zones (334 reflexions) taken together the reliability factor (R) was 0.094. The standard deviations of the coordinates are approximately 0.014 Å. The benzene rings of the benzoate groups are inclined to the plane of the anthracene nucleus at an angle of 110.5° . One of the bonds in the benzene ring has a value of 1.3 Å and there is an intermolecular distance between a hydrogen atom of this ring in one molecule and the centro-symmetrical hydrogen atom in another molecule of approximately 1.8 Å.

Introduction

The compound 9:10-anthrahydroquinone dibenzoate (Fig. 1) is of interest from a crystallographic point of view since it is a rather rare example, a fairly complicated organic substance which crystallizes in the triclinic system, with only one molecule per unit cell. Moreover, its structure includes an aromatic anthracene nucleus and two benzoic acid groups. It was first studied as one of a group of compounds derived from 9:10-dihydroxy-9:10-dihydroanthracene which were being investigated by Prof. E. Boyland at the

Chester Beatty Research Institute, London. Some of these appeared to have unexpected structural characteristics and it was considered useful to determine the molecular shape of this compound where the anthracene nucleus is aromatic.

Crystal data

The crystals are triclinic prismatic needles with a yellowish-green colour.

The unit cell was chosen so that the following conventions were obeyed. (1) The cell is the smallest having the full symmetry; (2) the axes are right-handed; (3) $c < a < b$; (4) α and β are obtuse.

$$\begin{aligned} a &= 8.91, b = 12.60, c = 5.83 \text{ \AA}; \\ \alpha &= 105.2^\circ, \beta = 106.5^\circ, \gamma = 58.2^\circ; \\ d(\text{obs.}) &= 1.314 \text{ g.cm.}^{-3}; d(\text{calc.}) = 1.316 \text{ g.cm.}^{-3}; \\ &\text{one molecule (C}_{28}\text{H}_{18}\text{O}_4) \text{ per unit cell}; \\ &\text{space group } P\bar{1}. \end{aligned}$$

Experimental

The unit-cell parameters were determined from oscillation and Weissenberg photographs and the intensities were estimated by visual methods from Weissenberg photographs with multiple-film packs to obtain the range of intensities required. Cu $K\alpha$ radiation was used throughout. The intensities of the equatorial layers of the three axial zones were measured as carefully as possible but since it proved impossible to solve the structure from these the most intense reflections $hk1$, $hk2$ and $hk3$ were measured. Although these latter reflections made it possible to determine the structure they were excluded from the subsequent refinement.

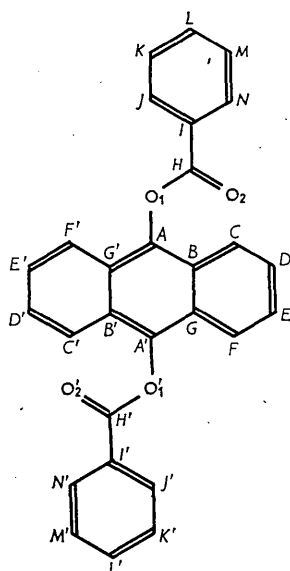


Fig. 1. Molecule of 9:10-anthrahydroquinone dibenzoate.

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Determination of the structure

The intensities of the $hk0$ reflections were tested by the statistical method of Howells, Phillips & Rogers (1950) and as can be seen from Fig. 2 there was no doubt about the symmetry of this zone. Accordingly the space group $P\bar{1}$ was assigned. With only one molecule in the unit cell this means that the molecule has a centre of symmetry and we can choose this as the origin of coordinates. With the aid of models of the unit cell and the molecule on the same scale the general disposition of the molecule in the cell was established. The molecule was approximately 18 Å long and less than 10 Å wide. The longest and shortest diagonals of the cell are 21 Å and 12 Å respectively. It was concluded from these figures that the anthracene nucleus lay roughly along the short diagonal and the line joining the centres of the benzoate groups was in the direction of the long diagonal of the cell. Examination of the $hk0$ weighted reciprocal lattice (Fig. 3) indicated a possible orientation for a 'benzene' ring. Since there appeared to be only six groups of spots which stood out in this way it might be assumed that the benzene rings of the benzoate groups were parallel to and similarly oriented to those of the anthracene nucleus but this assumption proved to be untenable. One remarkable feature of the $hk0$ zone was the absence of any observed intensity for the plane (110). This could be explained if the atoms were spread out fairly uniformly between adjacent (110) planes so that half gave a positive and half a negative contribution to the structure factor. Many attempts by 'trial and error' and with the optical-transform technique failed to give a satisfactory solution for the orientation of the two parts of the molecule. It seemed clear, however, from a detailed study of the optical transforms of an anthracene model and of a benzoate model that the most probable arrangement would be one in

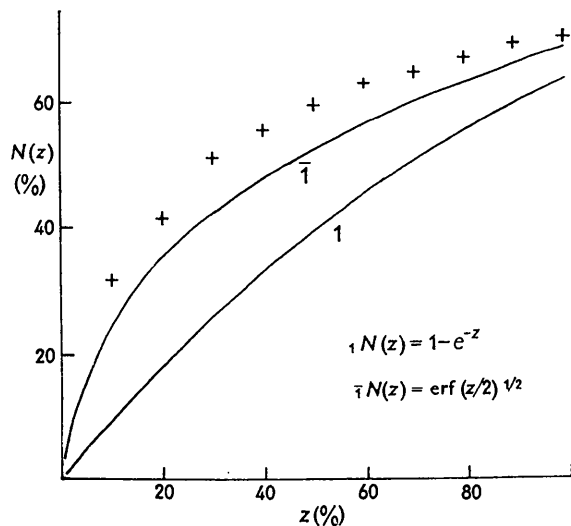


Fig. 2. Test for centre of symmetry ($hk0$ reflections).

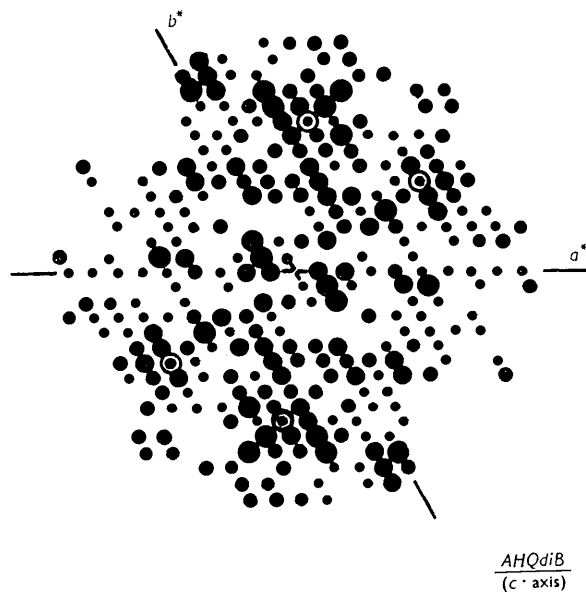


Fig. 3. $hk0$ weighted reciprocal lattice plane.

which the benzene ring of the benzoate group was inclined at almost 90° to those of the anthracene nucleus. During the course of this study of the optical transforms several ideas of more general interest related to their interpretation were developed and it is proposed to discuss these in a separate paper.

If the two components of the molecule were approximately at right angles to each other they would give rise to two separate 'columnar' transforms which might be recognized if a three-dimensional weighted reciprocal lattice was constructed. Although interference between the two transforms would occur confusion would be minimized if the reciprocal lattice was viewed along the 'columns' of each transform component in turn since in the appropriate direction one component would be resolved while the other would not. This was demonstrated by Kenyon & Taylor (1953) in the case of a known structure, naphthalene, but it is thought that this is the first use of this idea in solving an unknown structure.

The layers of the reciprocal lattice parallel to the $hk0$ layer were prepared on glass plates. (Some old unexposed photographic plates, $6\frac{1}{2} \times 4\frac{3}{8}$ inches) were fixed, washed and dried, and the reciprocal-lattice spots were drawn in Indian ink on the emulsion side). Two plates were prepared for each non-equatorial layer, one for $F(hkl)$ and one for $F(\bar{h}\bar{k}l)$ and the stack of plates assembled in their correct positions relative to each other.

The range of F values was divided into 5 groups and the weighted reciprocal lattice planes had spots of 5 graded sizes to correspond. Consequently for this purpose it is unnecessary to measure the intensities with a high accuracy. However, if the compound is an interesting and important one this is a short-sighted



Fig. 4. Photograph of 3-D weighted reciprocal lattice (a) in focus, (b) slightly out-of-focus showing peaks due to anthracene nucleus.

policy since subsequent refinement may be seriously hampered by the lack of accurate structure factors for upper layers. The model was illuminated by placing it over a viewing box and it was found helpful to look at it through almost closed eyelids; this causes the individual spots to coalesce. The effect is rather like taking a photograph slightly out-of-focus (see Figs. 4(a) and (b)). After some careful searching it was possible to recognize two transforms but at first it was impossible to say which corresponded to which molecular component. A little experimentation with the optical diffractometer soon supplied the solution.

In order to obtain approximate atomic coordinates it was found advisable to locate the intersections of the 'columns' of the 3-D transform with each of the $hk0$, $hk1$, $hk2$ and $hk3$ lattice layers in turn. Each set of columns is inclined to the layers, and therefore, on any particular layer, the six inner intersections, surrounding the central one, lie on an ellipse. A special technique for analyzing ellipses of this type was developed, and is described in the paper referred to above. By means of this it was possible to derive, from the ellipses, the values of the parameters φ , ω and ψ which define the respective orientations of the anthracene nucleus and the benzoate group with respect to the plane of the c -axis projection. The accuracy with which this can be done is illustrated in the case of the anthracene nucleus in Table 1.

Table 1. Values of the tilt parameters for anthracene nucleus derived from 3-D reciprocal lattice

Method of estimation	φ	ω	ψ
(1) 3-D lattice directly	55.0°	—	—
(2) From ellipses on sections through transform (means)	53.2°	9.2°	51.9°
(3) Values obtained from subsequent Fourier syntheses	54.5°	10.3°	50.6°

Having obtained the orientations of the separate components there remained the problem of fitting them together in the correct manner. There were 18 different combinations which would satisfy the chemical formula and the 3-D transform. Six of these

possible combinations seemed more probable than the remainder. Masks of each of the six were prepared and examined in the optical diffractometer and the optical transform compared with the $hk0$ weighted reciprocal lattice. It was not difficult to decide on the correct one. Atomic coordinates x and y could now be assigned to the atoms and assuming normal bond lengths and bond angles it was possible to derive z coordinates. Thus models representing the projection down the a and b axes could be constructed. In a triclinic cell this is far from straight-forward. Masks representing these projections were prepared and the optical transforms compared with the corresponding weighted reciprocal-lattice planes. The results are shown in Fig. 5. The agreement was not perfect but was sufficiently good to justify accepting the coordinates as approximately correct. With these x and y coordinates, 119 of the structure factors with the largest observed value were calculated and the resulting value of R ($=\sum|F_o| - |F_c|/\sum|F_o|$) was 0.52. Although this was a disappointing value the agreement of the over-all pattern of the reciprocal lattice plane with the optical transform justified the assumption that the signs of most of the larger structure factors were correct. A Fourier synthesis was computed with 90 F_o and although few atoms were resolved the general pattern of the molecule was clearly seen (Fig. 6). The position of the benzoate group had to be changed slightly from that postulated and with the new coor-

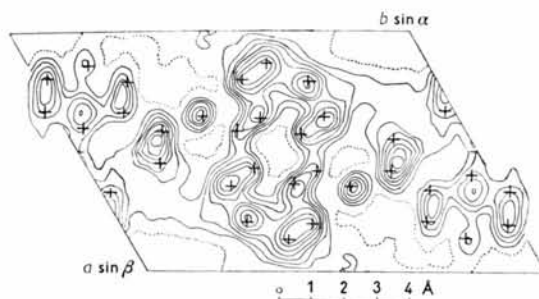


Fig. 6. First Fourier ($hk0$). The crosses indicate the original atomic positions which were derived directly from the study of the 3-D weighted reciprocal lattice.

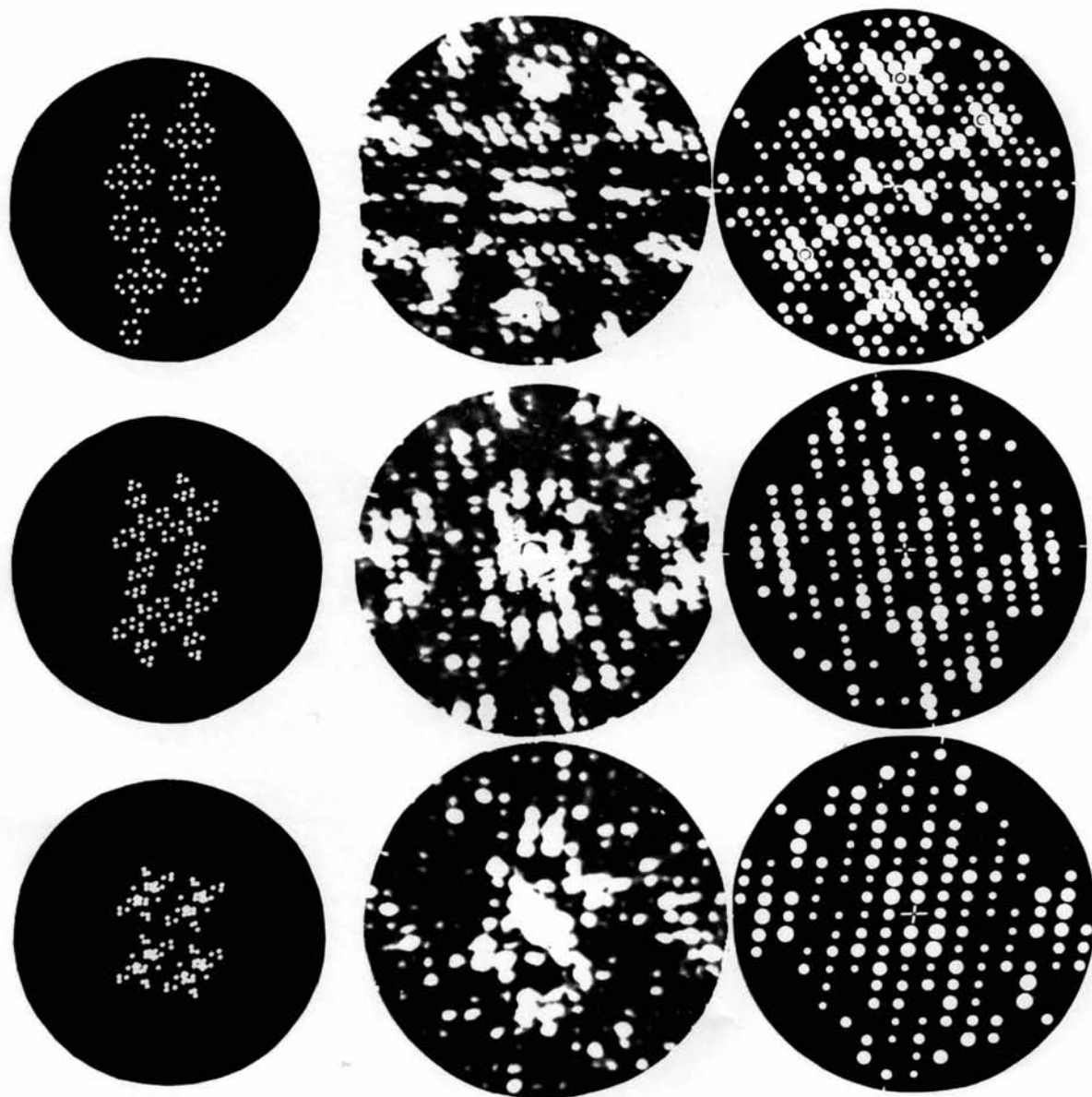


Fig. 5. Early models of molecule, corresponding weighted reciprocal lattice planes and optical transforms (a) $hk0$, (b) $0kl$, (c) $h0l$

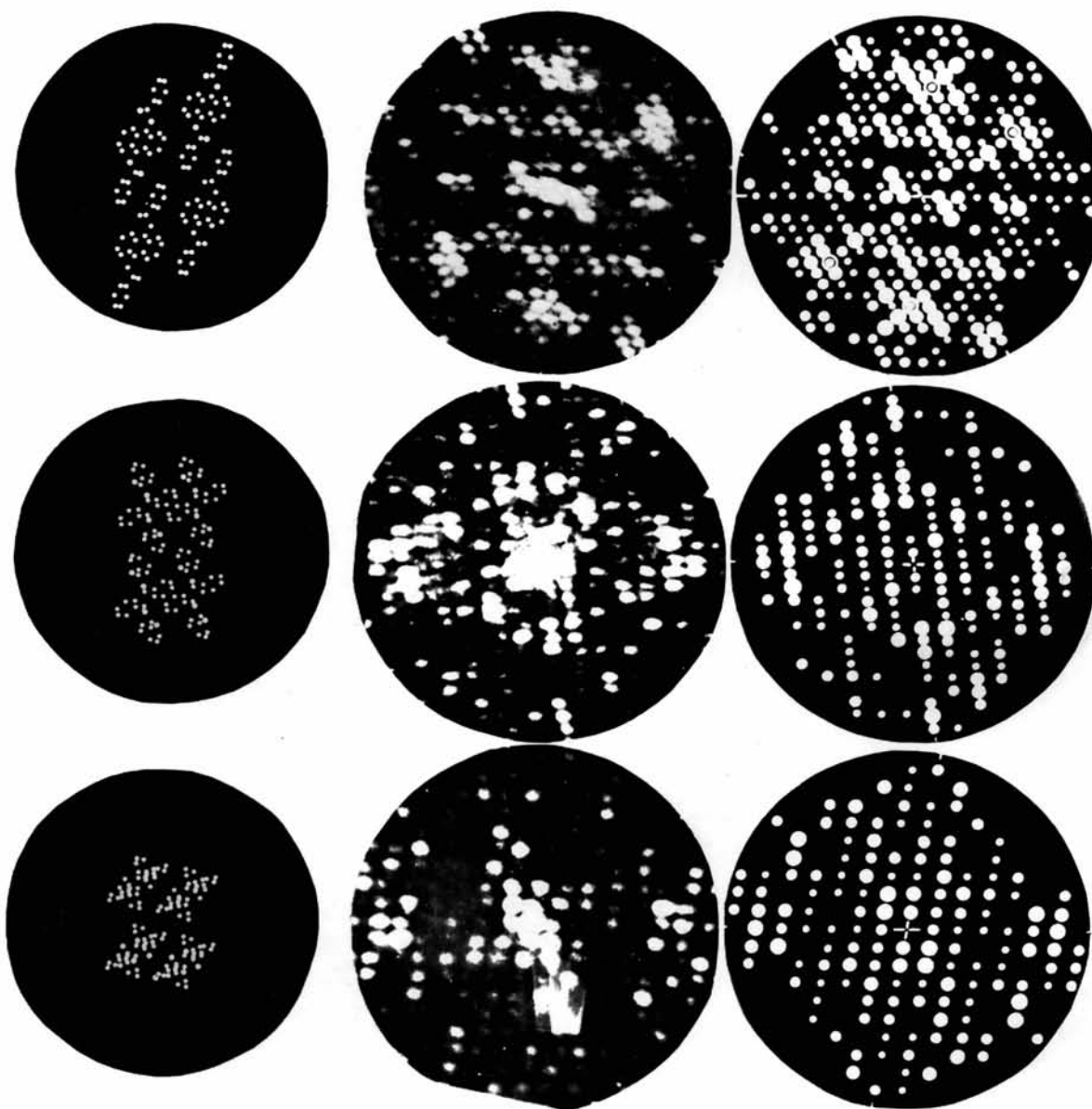


Fig. 8. Optical transforms for the final model (a) $hk0$, (b) $0kl$, (c) $h0l$.

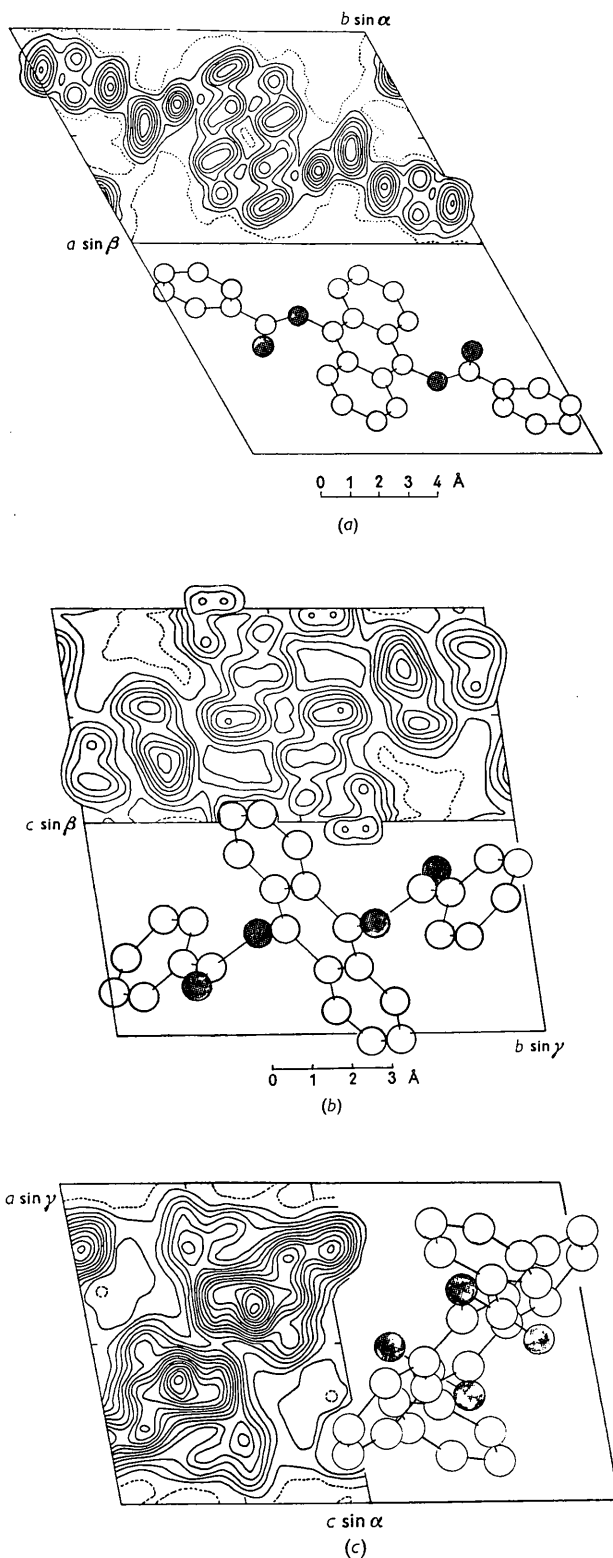


Fig. 7. Final Fourier projections. (a) $hk0$, (b) $0kl$, (c) $h0l$. Contours are at intervals of $1 \text{ e} \cdot \text{\AA}^{-2}$, the $1(e)$ contour is shown in broken line.

dinates the value of R for the same 119 planes as above dropped to 0.35. Because of the very considerable overlapping in the projection, estimation of atomic positions was difficult but by successive F_o and $(F_o - F_c)$ Fourier syntheses the value of R for the 231 $hk0$ reflections dropped to 0.22 and the temperature factor B was estimated to be 4.5 \AA^{-2} .

With the optical diffractometer as a check, z coordinates were derived on the basis of known bond-lengths. The calculated signs of 82 of the $0kl$ reflections were used with the F_o to compute a Fourier projection. Only six atoms were resolved but with a revised value of B , for this zone, of 5.65 \AA^{-2} and after two $(F_o - F_c)$ syntheses the value of $R(0kl)$ was 0.26. Combining the coordinates obtained from the two zones the $h0l$ structure factors were calculated. The value of $R(h0l)$ was 0.26 and again a temperature factor (B) of 5.65 \AA^{-2} was indicated. The structure factors were recalculated and reduced to a standard scale for all three zones. The final F_o Fourier maps are shown in Fig. 7 and the optical diffractometer patterns in Fig. 8. At this stage, the values of the reliability factors were

$$R(hk0) = 0.23; R(h0l) = 0.25; R(0kl) = 0.22.$$

Refinement by least squares

In the first place the $hk0$ zone was refined with isotropic temperature factors. This was made possible through the kindness of Dr Judith Milledge who had written the required program on the Ferranti 'Pegasus' machine. The first cycle reduced R to 0.19 and this was followed by an $(F_o - F_c)$ Fourier synthesis. Two more cycles of least-squares refinement reduced R to 0.17. It was fairly clear that in a structure such as this there would be considerable anisotropy in the thermal vibrations of some of the atoms so it was decided to use the structure factors for the three axial zones in a partial three-dimensional least-squares refinement with a programme which would treat each atom separately.

The three-dimensional anisotropic refinement was carried out on the Leeds University 'Pegasus' computer with the programme written by Dr D. W. J. Cruickshank. In the first place an $(F_o - F_c)$ Fourier synthesis was computed with the $h0l$ reflections in order to improve the coordinates of the x coordinates and to obtain confirmation of the individual isotropic temperature factors. There were 333 observed reflections and with the coordinates and isotropic temperature factors obtained as indicated above the value of $R(hkl)$ was 0.22. Some fairly considerable shifts in the carbon atom coordinates were indicated by the first cycle and applying these, but still using isotropic temperature factors, R dropped to 0.21. A further cycle reduced this to 0.16 but the output now gave anisotropic temperature parameters and the indicated parameter shifts were multiplied by 0.66 before being

Table 2. Carbon and oxygen atom coordinates (Å) and standard deviations (Å)

Atom	<i>x</i>	$\sigma(x)$	<i>y</i>	$\sigma(y)$	<i>z</i>	$\sigma(z)$
O1	(1.488)	1.464	0.007	(1.751)	1.769	0.007
O2	(0.071)	-0.018	0.008	(3.730)	3.746	0.008
A	(0.677)	0.697	0.011	(0.945)	0.917	0.010
B	(1.265)	1.289	0.009	(-0.050)	-0.081	0.010
C	(2.539)	2.580	0.012	(-0.151)	-0.174	0.012
D	(3.101)	3.119	0.012	(-1.121)	-1.165	0.013
E	(2.424)	2.435	0.015	(-2.066)	-2.146	0.013
F	(1.132)	1.151	0.012	(-2.041)	-2.045	0.012
G	(0.552)	0.602	0.010	(-1.071)	-1.039	0.010
H	(0.802)	0.912	0.011	(3.301)	3.273	0.011
I	(1.746)	1.763	0.010	(4.057)	4.084	0.010
J	(2.522)	2.617	0.014	(3.629)	3.571	0.012
K	(3.208)	3.369	0.015	(4.536)	4.430	0.018
L	(3.270)	3.229	0.016	(5.746)	5.707	0.013
M	(2.308)	2.416	0.014	(6.212)	6.188	0.011
N	(1.657)	1.662	0.012	(5.380)	5.372	0.012

used in the next cycle. Four further cycles of least-squares refinement reduced *R* to 0.094 for 334 reflections. For the individual zones the values were:

$$R(0kl) = 0.085, R(h0l) = 0.100, R(hk0) = 0.088.$$

The shifts in parameters had continued to oscillate in sign and for the last two cycles the indicated shifts were multiplied by 0.3. The final coordinates are given in Table 2 together with the estimated standard deviations. Because of the limited number of reflections used and also because only partial shifts were

allowed, the standard deviations are under-estimates and it would be reasonable to increase the ones given in the table by 50%. The values of the coordinates given in brackets are those obtained from two-dimensional F_o and $(F_o - F_c)$ Fourier syntheses before carrying out the least-squares refinement.

The calculated hydrogen coordinates are given in Table 3.

(A single isotropic temperature factor for the hydrogen atoms was included in the least-squares refinement.)

The temperature parameters (U_{ij}) and their standard deviations (σ) of the carbon atoms are given in Table 4,

Table 3. Calculated hydrogen coordinates (Å) and isotropic temperature factor (*B*)

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i>
C(H)	3.122	0.545	2.367	7.98
D(H)	4.073	-1.206	4.081	7.98
E(H)	2.875	-2.926	3.894	7.98
F(H)	0.613	-2.768	2.022	7.98
J(H)	2.683	2.567	-1.000	7.98
K(H)	4.010	4.087	-1.014	7.98
L(H)	3.763	6.339	0.734	7.98
M(H)	2.343	7.189	2.528	7.98
N(H)	1.019	5.726	2.670	7.98

$$\langle \bar{\mu}^2 \rangle = \sum_{i=1}^3 \sum_{j=1}^3 U_{ij} l_i l_j.$$

The observed and calculated structure factors are given in Table 5 (the structure factors for the unobserved reflexions were calculated in the last cycle but they were not included in the least-squares refinement).

Table 4. Temperature factors U_{ij} and standard deviations (σ) of the carbon and oxygen atoms (Å⁻²)

Atom	U_{11}	$\sigma(U_{11})$	U_{22}	$\sigma(U_{22})$	U_{33}	$\sigma(U_{33})$	U_{12}	$\sigma(U_{12})$	U_{23}	$\sigma(U_{23})$	U_{13}	$\sigma(U_{13})$
O1	0.0776	0.0037	0.0655	0.0033	0.0742	0.0040	-0.0966	0.0062	0.0186	0.0089	0.0378	0.0100
O2	0.0997	0.0047	0.0763	0.0038	0.1121	0.0056	-0.1189	0.0077	-0.0093	0.0110	0.1006	0.0126
A	0.0730	0.0051	0.0583	0.0045	0.0920	0.0069	-0.0809	0.0086	0.0054	0.0144	0.0627	0.0168
B	0.0517	0.0042	0.0569	0.0042	0.0867	0.0064	-0.0602	0.0079	-0.0075	0.0135	0.0359	0.0140
C	0.0754	0.0057	0.0871	0.0066	0.0898	0.0068	-0.1011	0.0108	0.0125	0.0191	0.0440	0.0158
D	0.0799	0.0061	0.0869	0.0067	0.0934	0.0072	-0.0863	0.0120	-0.0008	0.0178	0.0253	0.0180
E	0.0941	0.0068	0.0792	0.0059	0.0937	0.0072	-0.0761	0.0121	0.0076	0.0168	0.0459	0.0181
F	0.0770	0.0056	0.0680	0.0051	0.0931	0.0074	-0.0843	0.0097	0.0250	0.0152	-0.0174	0.0182
G	0.0604	0.0048	0.0582	0.0044	0.0892	0.0067	-0.0716	0.0085	-0.0126	0.0136	0.0422	0.0154
H	0.0687	0.0050	0.0688	0.0049	0.0764	0.0062	-0.0790	0.0094	-0.0153	0.0144	0.0193	0.0150
I	0.0684	0.0047	0.0591	0.0042	0.0686	0.0055	-0.0880	0.0084	0.0246	0.0124	0.0322	0.0133
J	0.0967	0.0068	0.0829	0.0059	0.0763	0.0060	-0.1128	0.0118	0.0400	0.0145	0.0554	0.0167
K	0.1116	0.0086	0.1367	0.0102	0.0955	0.0078	-0.1599	0.0163	-0.0022	0.0230	0.0627	0.0201
L	0.1232	0.0089	0.0870	0.0069	0.1394	0.0116	-0.1376	0.0147	0.0399	0.0225	0.0445	0.0297
M	0.1073	0.0075	0.0690	0.0055	0.1126	0.0088	-0.1096	0.0117	0.0149	0.0164	0.0995	0.0196
N	0.0856	0.0064	0.0746	0.0057	0.1131	0.0087	-0.1023	0.0109	0.0285	0.0172	0.0681	0.0197

(It should be noted that the above are the parameters as used in the least-squares programme and U_{12} , U_{22} , U_{13} are each the sum of the two corresponding off-diagonal terms in the *U* tensor).

Table 5. Observed and calculated structure factors

$h\ 0\ l$																	
$h\ l$	F _o	F _c	$h\ l$	F _o	F _c	$h\ l$	F _o	F _c	$h\ l$	F _o	F _c	$h\ l$	F _o	F _c	$h\ l$	F _o	F _c
1 0	38.3	38.4	1 1	28.4	-32.6	1 2	15.0	-17.1	2 3	6.5	-6.0	3 4	2.6	2.6	4 5	<0.9	-0.4
2 0	32.5	-29.0	2 1	20.6	-22.1	2 2	16.3	-16.0	3 3	1.9	-1.0	4 4	<1.3	1.5	5 5	1.2	-1.0
3 0	6.1	5.6	3 1	15.8	-15.4	3 2	3.6	-3.6	4 3	2.4	2.3	5 4	<1.1	1.0	6 6	2.4	2.5
4 0	9.6	-9.4	4 1	9.0	-7.2	4 2	1.2	-1.9	5 3	1.2	0.2	6 4	<0.9	0.0	1 6	1.6	1.2
5 0	4.8	-3.7	5 1	4.1	4.0	5 2	<1.3	-0.5	6 3	<1.1	1.1	7 4	<0.6	-0.1	2 6	0.9	-0.9
6 0	2.5	2.7	6 1	<1.3	0.9	6 2	2.3	-2.6	7 3	<0.9	1.1	8 5	2.6	2.9	3 6	1.7	-1.4
7 0	1.3	1.4	7 1	1.8	-1.5	7 2	1.0	-0.7	8 3	<0.6	0.1	1 5	7.3	5.8	4 6	<0.6	-0.6
8 0	1.0	-0.4	8 1	1.7	-1.5	8 2	1.0	0.6	0 4	1.1	0.9	2 5	<1.3	-0.4	0 7	0.7	0.8
9 0	1.0	-1.1	9 1	<0.6	-0.2	0 3	6.1	6.2	1 4	0.9	0.8	3 5	<1.1	-0.4	1 7	<0.6	0.2
0 1	20.7	21.5	0 2	5.5	5.2	1 3	3.5	3.8	2 4	2.1	1.7						

$h\ 0\ l$																	
$h\ l$	F _o	F _c	$h\ l$	F _o	F _c	$h\ l$	F _o	F _c	$h\ l$	F _o	F _c	$h\ l$	F _o	F _c	$h\ l$	F _o	F _c
1 1	55.2	60.8	1 2	12.3	-13.0	1 3	0.9	0.2	1 4	1.5	1.3	1 5	4.5	-4.0	2 6	1.9	1.4
2 1	37.2	43.3	2 2	4.7	-4.3	2 3	5.2	5.2	2 4	1.1	0.8	2 5	0.8	0.7	3 6	0.8	-0.9
3 1	7.0	-6.2	3 2	15.0	15.5	3 3	4.2	4.1	3 4	3.0	-2.6	3 5	1.9	-1.9	4 6	0.7	-0.8
4 1	16.3	-13.7	4 2	8.4	-8.2	4 3	1.0	1.2	4 4	0.8	-1.3	4 5	4.9	-5.5	5 6	0.7	-0.6
5 1	0.9	-0.4	5 2	6.8	-6.3	5 3	1.8	1.8	5 4	<1.3	0.5	5 5	3.1	-2.6	6 6	1.1	-0.9
6 1	2.0	-2.1	6 2	2.6	2.4	6 3	2.3	2.4	6 4	1.5	0.9	6 5	0.7	-0.9	1 7	0.7	0.5
7 1	2.0	-2.2	7 2	<1.3	-1.1	7 3	3.2	3.2	7 4	1.1	1.4	7 5	<0.9	-0.3	2 7	1.5	1.6
8 1	1.0	-1.0	8 2	2.4	-2.6	8 3	<0.9	-0.3	8 4	<0.9	0.5	8 5	<0.6	-0.6	3 7	1.0	0.8
9 1	0.8	-1.1	9 2	<0.9	-0.7	9 3	<0.7	-1.2	9 4	<0.4	-0.3	1 6	2.7	2.4	4 7	0.5	-0.4

$0\ k\ l$																	
$k\ l$	F _o	F _c	$k\ l$	F _o	F _c	$k\ l$	F _o	F _c	$k\ l$	F _o	F _c	$k\ l$	F _o	F _c	$k\ l$	F _o	F _c
1 0	20.7	20.1	1 1	26.8	-29.5	1 2	14.0	14.6	1 3	1.6	-1.1	2 4	2.2	-2.2	4 5	1.0	1.0
2 0	8.3	7.8	2 1	12.6	13.5	2 2	4.7	-4.7	2 3	9.7	-10.1	3 4	5.5	-5.2	5 5	1.4	1.7
3 0	3.1	3.1	3 1	17.2	18.5	3 2	2.4	-2.4	3 3	9.6	-9.7	4 4	2.5	-2.4	6 5	<0.9	-0.4
4 0	3.9	4.1	4 1	4.8	-4.3	4 2	9.5	-9.7	4 3	1.9	-1.6	5 4	3.4	-3.2	7 5	<0.9	0.1
5 0	17.7	-18.2	5 1	19.3	-17.6	5 2	1.9	2.2	5 3	0.9	-0.5	6 4	<1.3	-0.0	8 5	<0.9	0.6
6 0	8.5	7.5	6 1	9.5	8.3	6 2	<1.1	0.1	6 3	1.7	1.6	7 4	<1.3	-0.6	1 6	1.8	2.3
7 0	11.2	10.3	7 1	2.1	-1.8	7 2	3.7	-3.8	7 3	3.4	2.7	8 4	<1.3	-0.2	2 6	1.4	-1.3
8 0	2.4	-2.4	8 1	<1.1	1.0	8 2	1.9	-1.9	8 3	<1.5	1.4	9 4	<0.9	-0.3	3 6	<0.9	-0.2
9 0	1.7	-1.3	9 1	1.8	1.7	9 2	4.4	-5.1	9 3	2.5	-2.2	10, 4	<0.6	-0.1	4 6	<0.9	0.7
10, 0	1.1	1.1	10, 1	2.6	-3.1	10, 2	3.5	-3.7	10, 3	<0.9	-0.4	1 5	4.4	5.3	5 6	<0.7	-0.4
11, 0	2.0	2.1	11, 1	<1.1	-0.3	11, 2	1.0	1.1	11, 3	<0.7	-0.8	2 5	4.0	-4.3	6 6	<0.4	-0.5
12, 0	3.8	3.6	12, 1	<0.9	0.3	12, 2	<0.7	-0.3	1 4	4.1	4.3	3 5	1.6	-1.6	1 7	<0.6	-0.5
13, 0	1.8	1.8	13, 1	0.7	1.0												

$0\ k\ l$																	
$k\ l$	F _o	F _c	$k\ l$	F _o	F _c	$k\ l$	F _o	F _c	$k\ l$	F _o	F _c	$k\ l$	F _o	F _c	$k\ l$	F _o	F _c
1 1	11.6	14.7	1 2	12.8	17.5	1 3	3.2	-3.1	1 4	1.2	-1.0	2 5	6.3	7.8	3 6		
2 1	35.0	-38.4	2 2	4.1	-4.6	2 3	9.2	9.5	2 4	1.0	1.0	3 5	4.0	4.6	4 6	<1.1	-1.3
3 1	10.6	10.7	3 2	14.4	-14.2	3 3	1.4	1.5	3 4	2.8	2.9	4 5	<1.3	-2.5	5 6	<0.9	-1.1
4 1	4.6	-4.4	4 2	22.3	-23.0	4 3	7.0	-6.8	4 4	3.8	-3.9	5 5	1.2	-1.2	6 6	<0.9	0.6
5 1	6.2	-6.5	5 2	5.3	-4.6	5 3	<0.9	-3.1	5 4	1.3	-0.7	6 5	<1.3	0.9	7 6	<0.9	-0.7
6 1	16.0	-16.4	6 2	<0.9	-1.8	6 3	<0.9	1.6	6 4	<1.3	-1.1	7 5	<1.1	0.3	8 6	<0.7	-0.6
7 1	<0.9	2.0	7 2	4.2	3.7	7 3	2.1	2.4	7 4	<1.3	-0.4	8 5	1.5	1.4	9 6	<0.6	0.5
8 1	<1.1	0.4	8 2	1.1	1.4	8 3	1.7	-1.7	8 4	<1.3	0.8	9 5	<0.9	0.5	1 7	<0.6	0.1
9 1	<1.3	-0.4	9 2	2.1	2.0	9 3	3.5	-3.5	9 4	1.9	-1.6	10, 5	<0.7	-0.8	2 7	<0.6	0.4
10, 1	<1.3	-1.1	10, 2	<1.3	-1.1	10, 3	0.9	-0.2	10, 4	<0.9	1.3	11, 5	<0.6	0.2	3 7	<0.6	0.5
11, 1	<1.3	-0.6	11, 2	<1.1	-1.2	11, 3	2.1	-2.6	11, 4	<0.9	0.1	1 6	1.5	-1.9	4 7	<0.6	-0.6
12, 1	1.3	-1.4	12, 2	1.3	-1.7	12, 3	1.2	-1.2	12, 4	<0.6	-1.1	2 6	<1.1	0.5	5 7	<0.6	-1.0
13, 1	<0.7	0.6	13, 2	<0.7	0.8	13, 3	<0.6	-0.0	1 5	4.0	4.5						

Discussion of the structure

One of the main interests in this molecule is the relation between the anthracene nucleus and the benzoate groups. The mean plane of all the carbon atoms in the anthracene nucleus (*A, B, C, D, E, F, G*) was computed and in addition that of the carbon

atoms of one of the benzoate groups (*H, I, J, K, L, M, N*). In order to do this it is convenient to choose rectangular axes; these were as follows. *y'* is parallel to *b*, *x'* is in the *xy* plane and is perpendicular to *b*, *z'* is perpendicular to (001). The relation between the rectangular coordinates (*x', y', z'*) and the triclinic ones (*x, y, z*) is given by

Table 5 (cont.)

$h k 0$																					
h	k	Fo	Fc	h	k	Fo	Fc	h	k	Fo	Fc	h	k	Fo	Fc	h	k	Fo	Fc		
1	1	<0.4	-0.6	6	3	3.0	-2.4	2	6	15.1	-12.5	6	8	1.2	-1.3	1,11	1.8	1.1	4,13	<1.1	-0.5
2	1	4.0	-3.9	7	3	1.8	-1.5	3	6	17.6	-15.1	7	8	2.6	2.5	2,11	5.0	4.3	5,13	2.9	-2.7
3	1	8.0	-7.9	8	3	1.9	-1.8	4	6	2.7	2.9	8	8	3.4	3.3	3,11	7.9	7.3	6,13	<1.1	-0.7
4	1	1.7	-1.4	9	3	<0.9	0.3	5	6	<0.9	0.1	9	8	<1.1	-0.1	4,11	6.7	-6.5	7,13	1.7	0.9
5	1	7.1	-7.0	1	4	2.4	-2.3	6	6	2.1	2.5	1	9	5.2	-5.3	5,11	8.2	-8.3	8,13	2.5	2.4
6	1	1.8	-2.1	2	4	11.1	-10.6	7	6	13.5	14.1	2	9	1.2	-1.1	6,11	<1.1	-0.2	9,13	<0.9	0.7
7	1	<1.1	0.4	3	4	19.5	17.7	8	6	6.6	6.3	3	9	9.4	-8.7	7,11	<1.1	0.3	1,14	2.5	3.0
8	1	<1.1	-0.0	4	4	8.3	8.6	9	6	1.6	-2.3	4	9	8.1	-7.4	8,11	<1.1	0.9	2,14	1.2	1.6
9	1	<1.1	0.4	5	4	18.9	-16.7	1	7	8.0	7.3	5	9	11.6	10.5	9,11	2.0	-1.6	3,14	0.7	0.1
1	2	30.7	29.3	6	4	1.1	1.4	2	7	<0.9	1.0	6	9	3.2	3.5	1,12	4.3	4.1	4,14	1.3	0.8
2	2	34.3	-31.3	7	4	9.8	9.6	3	7	13.7	-10.1	7	9	2.9	-2.9	2,12	<1.1	-0.7	5,14	1.0	-0.8
3	2	1.2	1.1	8	4	2.4	2.4	4	7	3.1	3.0	8	9	1.1	-1.6	3,12	5.2	-4.8	6,14	1.4	-1.0
4	2	1.7	-1.7	9	4	1.5	1.6	5	7	7.3	5.6	9	9	2.9	-2.7	4,12	3.3	-3.1	7,14	1.9	2.0
5	2	5.0	-5.1	1	5	15.6	-14.5	6	7	3.5	3.3	1,10	1.4	1.4	-1.3	5,12	3.4	-3.9	8,14	<0.9	0.2
6	2	1.5	1.2	2	5	18.9	-15.4	7	7	8.7	8.8	2,10	2.6	-2.9	0,12	5.4	-4.4	9,14	2.0	-2.6	
7	2	1.7	-1.7	3	5	22.8	-20.6	8	7	4.1	4.4	3,10	7.1	6.9	7,12	<1.1	-0.3	3,15	<0.7	-0.4	
8	2	2.3	-2.1	4	5	21.3	-19.5	9	7	1.3	0.5	4,10	18.2	16.5	8,12	<1.1	-0.5	4,15	1.1	-1.5	
9	2	1.7	-1.8	5	5	7.0	-6.9	1	8	1.9	-1.7	5,10	2.7	2.5	9,12	1.5	-1.5	5,15	1.2	-1.0	
1	3	6.3	5.9	6	5	6.2	6.4	2	8	9.3	-7.8	6,10	4.5	-4.5	1,13	3.2	3.5	6,15	1.6	0.5	
2	3	10.2	9.8	7	5	10.4	9.7	3	8	8.2	-7.2	7,10	<1.1	-0.4	2,13	1.3	1.7	7,15	1.7	-1.5	
3	3	14.8	13.0	8	5	3.6	3.8	4	8	5.6	-5.4	8,10	<1.1	0.3	3,13	1.1	1.2				
4	3	20.5	19.4	9	5	1.6	-0.8	5	8	5.7	-6.2	9,10	<1.1	0.5							
5	3	8.9	9.1	1	6	13.4	12.9														

$h k 0$																							
h	k	Fo	Fc	h	k	Fo	Fc	h	k	Fo	Fc	h	k	Fo	Fc	h	k	Fo	Fc				
1	1	46.7	46.6	4	2	5.3	-6.5	8	3	<0.7	0.1	5	5	<1.1	0.3	3	7	3.7	-3.3	3	9	<0.9	-0.0
2	1	13.6	11.8	5	2	1.9	-1.3	1	4	2.4	3.0	6	5	<0.9	-0.5	4	7	<1.1	-1.2	4	9	<0.9	0.1
3	1	3.1	-3.3	6	2	1.2	-1.1	2	4	1.8	1.4	7	5	<0.7	0.5	5	7	<1.1	0.5	1,10	1.3	1.5	
4	1	14.7	-13.6	7	2	<1.1	-0.0	3	4	2.4	2.7	1	6	11.7	-11.6	6	7	1.9	2.6	2,10	0.7	0.9	
5	1	11.9	-10.3	8	2	<0.9	-0.0	4	4	2.3	2.8	2	6	10.6	-9.7	1	8	2.7	-2.5	3,10	<0.9	0.5	
6	1	<1.1	1.0	1	3	4.5	3.8	5	4	1.4	-1.3	3	6	1.4	-1.3	2	8	1.3	-1.4	4,10	<0.4	-0.3	
7	1	1.8	1.7	2	3	12.4	11.1	6	4	1.4	-1.7	4	6	2.2	1.9	3	8	<1.1	-0.5	1,11	<0.9	-0.4	
8	1	<1.1	-0.6	3	3	3.3	3.1	7	4	<0.9	0.7	5	6	0.8	1.4	4	8	<1.1	-0.7	2,11	<0.9	-0.2	
9	1	1.5	-1.6	4	3	3.3	-3.9	1	5	2.2	-2.7	6	6	1.4	1.7	5	8	<0.7	-0.6	3,11	<0.6	0.3	
1	2	45.6	-45.1	5	3	0.9	0.7	2	5	4.8	-4.5	1	7	3.3	3.9	1	9	1.0	-0.7	1,12	<0.9	0.3	
2	2	2.0	1.6	6	3	1.7	1.9	3	5	4.5	-4.0	2	7	7.0	-6.6	2	9	0.7	-0.9	2,12	0.7	-0.8	
3	2	3.2	-1.2	7	3	<1.1	0.5	4	5	1.7	1.6												

$$\begin{aligned}x' &= x \sin \gamma - z \cos \beta^* \sin \alpha, \\y' &= z \cos \alpha + x \cos \gamma + y, \\z' &= z \sin \beta^* \sin \alpha.\end{aligned}$$

The two parts of the molecule will be discussed separately.

(i) *Anthracene nucleus*

Referred to the rectangular axes defined above the mean plane of atoms *A, B, C, D, E, F* and *G* and of

the centro-symmetrically related atoms, is given by

$$0.7744x' - 0.3111y' - 0.5509z' = 0.$$

The deviations of the atoms from this plane are listed in Table 6.

The oxygen atom O1 is not quite in this plane but lies very close to it while the other oxygen atom is well away from the plane. The deviations of the carbon atoms are probably not significant.

(ii) *The benzene ring of the benzoate group*

With reference to the same rectangular axes the equation of the mean plane of atoms *H, I, J, K, L, M, N* is,

$$-0.7261x' + 0.3581y' - 0.5870z' + 0.2726 = 0.$$

The rectangular coordinates and deviations from this plane are given in Table 7.

The carbon atoms of the benzene ring itself are in the plane to within the experimental error but atom *H* is probably slightly out of the plane. The two oxygen atoms are on opposite sides of the plane.

Table 6. *Rectangular coordinates (Å) and deviations (Å) from the mean plane of the carbon atoms in the anthracene nucleus*

Atom	x'	y'	z'	Δ
O1	1.214	2.499	0.147	+0.082
O2	-0.338	3.294	1.595	-2.165
A	0.576	1.262	0.082	+0.008
B	0.878	0.301	1.074	-0.005
C	1.756	0.587	2.162	-0.014
D	2.032	-0.371	3.063	+0.001
E	1.468	-1.688	2.977	+0.022
F	0.578	-1.987	1.977	-0.023
G	0.313	-0.994	0.982	+0.011

Table 7. Rectangular coordinates (A) and deviations (Δ) from the mean plane of the carbon atoms of the benzoate group

Atom	x'	y'	z'	Δ
O1	—	—	—	-0.346
O2	—	—	—	+0.216
H	0.597	3.510	0.879	+0.035
I	1.333	4.787	0.815	-0.005
J	2.272	5.016	-0.235	+0.012
K	2.909	6.268	-0.225	-0.008
L	2.597	7.207	0.727	-0.004
M	1.717	7.000	1.663	+0.011
N	1.058	5.762	1.752	-0.006

The angle between the two planes is $110^\circ 30'$.

Bond lengths

The bond lengths and bond angles are given in Fig. 9. The bonds in the anthracene nucleus do not call for comment as there are no unusual or unexpected features. However, the bonds in the benzoate group are most unexpected. In particular the bond LM is only 1.302 \AA and even if we accept that the standard deviation of coordinates listed in Table 2 should be increased by 50% it seems im-

probable that the error in determining the length of this bond is as much as 0.08 \AA . The mean length of the bonds in this ring is 1.382 \AA which is slightly less than expected. The fact that all the other bonds in the whole molecule are of normal length would seem to suggest that the bond $L-M$ is not in error by more than $\pm 0.4 \text{ \AA}$ which would still make the length 1.34 \AA , a very considerable reduction compared with the mean bond length. The suggestion which is put forward in explanation is that the influence of the $C=O$ bond of the carboxyl groups is more profound when no hydrogen bonds are involved.

In addition, as pointed out below, there are very short intermolecular distances, between neighbouring molecules, which involve the hydrogen atoms attached to the atom N in each molecule. This distance 1.8 \AA is so short that, if correct, it indicates an intermolecular binding very different from normal van der Waals forces. The benzene ring, under these circumstances would not be truly aromatic and there could then be a rational explanation for a reduction in the length of one of the bonds in the ring.

It will be noticed that the two single $C-O$ bonds $H-O1$ (1.392) and $A-O1$ (1.394) are in excellent agreement and that the double bond $H-O2$ is the expected length (1.197). The spatial arrangement of the $H-O2$ bond in relation to the benzene ring may be significant. The two oxygen atoms are close to the plane of the ring (Table 7) and the double bond is on the same side of the line HIL as the short bond LM .

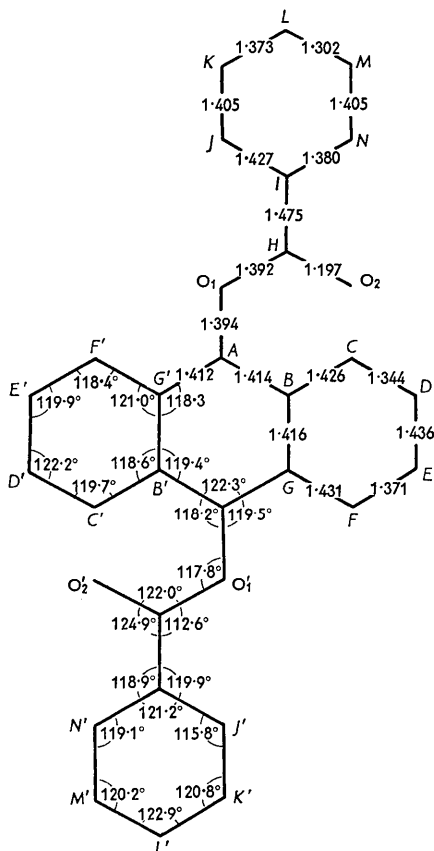


Fig. 9. Bond lengths (\AA) and bond angles.

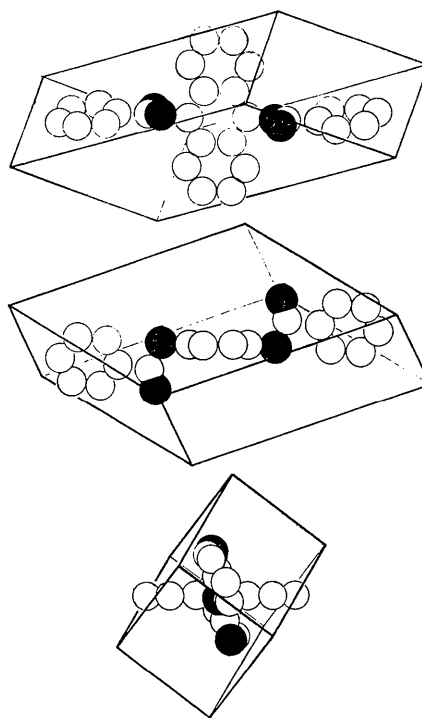


Fig. 10. Diagrams of the way the molecule is placed in the unit cell.

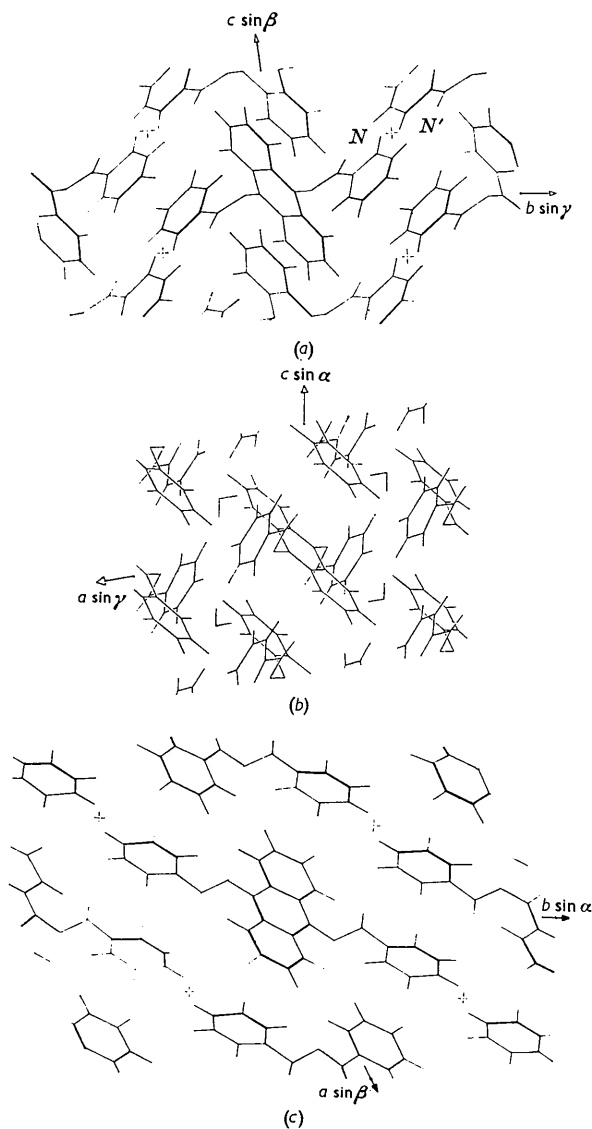


Fig. 11. Diagrams showing the relationship of the molecule to its neighbours.

Intermolecular distances

The arrangement of the molecule in the triclinic cell is shown in Fig. 10 and the relation of one molecule to its neighbours in Fig. 11. The shortest distance between atoms in neighbouring molecules is 1.785 Å between the hydrogen attached to atom *N* of the molecule at (0, 0, 0) and the symmetrically related hydrogen atom attached to atom *N'* of the molecule

at a diagonal translation (0, *b*, *c*). These atoms are indicated in Fig. 11. In the calculation of this distance it has been assumed that the hydrogens are symmetrically situated in the plane of the benzene ring and that the C–H bond-length is 1.0 Å. However, the inaccuracy in locating the position of the hydrogen atoms will have no appreciable effect on this remarkably short intermolecular distance unless of course the hydrogens are so far from their assumed positions that all previous assumptions about the shape of a benzene ring are invalid in respect to this compound

Table 8. *Intermolecular distances*

Molecule at (0, 0, 0)	Molecule at (0, 0, 1)	Distance (Å)
<i>F</i>	<i>B'</i>	3.501
<i>G</i>	<i>E'</i>	3.403
<i>B</i>	<i>F'</i>	3.501
<i>G</i>	<i>F'</i>	3.513
<i>C</i>	<i>J</i>	3.242

	Molecule at (0, 1, 1)	Distance (Å)
<i>N</i>	<i>O2'</i>	3.440
<i>M</i>	<i>O2'</i>	3.388
<i>N(H)</i>	<i>O2'</i>	2.820
<i>M(H)</i>	<i>O2'</i>	2.671
<i>N(H)</i>	<i>N'</i>	2.739
<i>N(H)</i>	<i>N(H)'</i>	1.785

The intermolecular distances which are less than 3.60 Å are listed in Table 8. Apart from distances involving hydrogen atoms the shortest intermolecular distances appear to be between carbon atom *M* of the molecule at (0, 0, 0) and the oxygen *O2'* of the molecule at (0, 1, 1). Several carbon–carbon distances of approximately 3.5 Å are observed and one of 3.4 Å.

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