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The Crystal Structure of 1:5-Dichloroanthraquinone

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The crystal structure of 1:5-dichloroanthraquinone has been determined by Fourier projections and line syntheses, and has been refined by difference syntheses. Small distortions from planarity in the molecule are shown to take place in the central ring, the outer rings including the chlorine atoms remaining planar. The symmetry is monoclinic, space group $P2_1/a$, and the cell dimensions are:

$$a = 11{\cdot}01,\quad b = 13{\cdot}06,\quad c = 3{\cdot}84\ \text{Å},\quad \beta = 92°\ 07'\,.$$

There are two molecules in the unit cell.

Introduction

The crystal-structure determination of anthraquinone by Sen (1948) has shown that within the accuracy of the determination the molecule is planar. However, little is known about the configuration of substituted anthraquinones, which constitute an important group of dyes. Of particular interest are the distortions which necessarily occur when the substitution is in one or more of the 1, 4, 5 and 8 positions, in order to give sufficient clearance between a substituting atom or group and the adjacent quinonoid oxygen atom. In the case of 1:5-dichloroanthraquinone a preliminary determination of the unit cell size and of the space group ($P2_1/a$) showed that since there are only two molecules in the unit cell, the molecule itself must possess a centre of symmetry. This permits a chair-shaped distortion of the central ring, but eliminates the boat-shape. The structure has been determined to investigate the precise nature of the distortion and non-planarity of the molecule.

Experimental

Long lath-shaped crystals of 1:5-dichloroanthraquinone with marked oblique cleavage were obtained by recrystallization from the melt of a pure finely divided sample between microscope slides. The unit cell is monoclinic, space group $P2_1/a$, and has dimensions

$$a = 11{\cdot}01,\quad b = 13{\cdot}06,\quad c = 3{\cdot}84\ \text{Å},\quad \beta = 92°\ 07'.$$

The density calculated for 2 molecules in the unit cell is 1·661 g.cm.$^{-3}$. Experimental density (by flotation in NaI solution) is 1·63 g.cm.$^{-3}$.

Intensity data for the [*c*] zero, first, and second layers, and the [*b*] zero layer, were recorded on Weissenberg photographs, using Cu $K\alpha$ radiation. A long and a short exposure, with three superimposed films, were taken for each zone, and the intensities were estimated visually by comparison with a calibrated scale of time exposures from the same crystal. Since every reflexion of measurable blackening was estimated on each film, for the majority of reflexions the intensity was the average value obtained from three or four estimations.

McWeeny's scattering factor curves (1951) for carbon and oxygen were incorporated in the structure-factor calculations. The scale factor and an average overall temperature factor were evaluated after refinement by plotting log (F_o/F_c) against $4 \sin^2 \theta$.

Structure determination

The short needle axis of 3·84 Å limits the inclination of the molecule from the (001) plane to within about 30°, but as the outline of the molecule is an ellipse of low eccentricity there are several reasonable packing arrangements in the plane.

The molecular-transform method (Knott, 1940) was used to determine the orientation of the molecule in the (001) plane. For the purpose of calculation the molecule was assumed to consist of three planar regular hexagons of side 1·4 Å, and the C=O and C–Cl bond lengths were taken as 1·2 Å and 1·7 Å respectively. The transform (Fig. 1) was calculated at intervals of $\frac{1}{16}$ reciprocal units along x^* and $\frac{1}{42}$ reciprocal units along y^*, using Beevers–Lipson strips for all the carbon contributions, and then adding the individually calculated oxygen and chlorine contributions. Differences in scattering power were allowed for by weighting the C, O, and Cl atomic centres in the ratio 6:8:17; but differences in shape of the scattering curves were neglected.

The best fit of the $hk0$ reciprocal lattice on the transform was found by first considering the three very strong planes (060), (230) and (590). The signs of 46 of the strongest $hk0$ reflexions were determined (contributions from the two molecules summed when $h+k$ is even, and subtracted when $h+k$ is odd) and

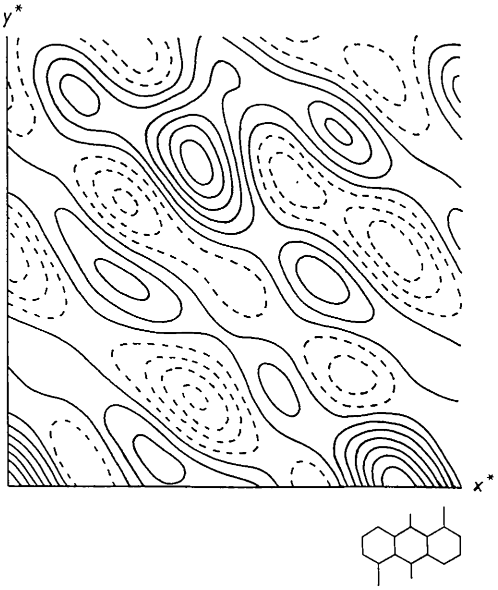

Fig. 1. Molecular transform of the molecule. Positive and zero contours full lines, negative contours broken lines.

were incorporated in a [c] Fourier projection, which gave resolution of all the atoms. Four further refinements by Fourier projections were carried out, the final one (Fig. 2) including 185 terms out of a possible 191. The centres of the peaks were located analytically by least squares, assuming a Gaussian electron-density distribution of the form $\varrho(x, y) = \exp(r-sx^2-ty^2-ux-vy-wxy)$. The temperature factor B in the expression $F_o \propto F_c \exp(-B \sin^2 \theta/\lambda^2)$ was estimated by plotting $\log(F_o/F_c)$ against $4 \sin^2 \theta$, giving a value of $B = 5{\cdot}8$ Å^2 averaged over all the atoms. The R factor at this stage was 0·170.

Further refinement of the x and y coordinates was

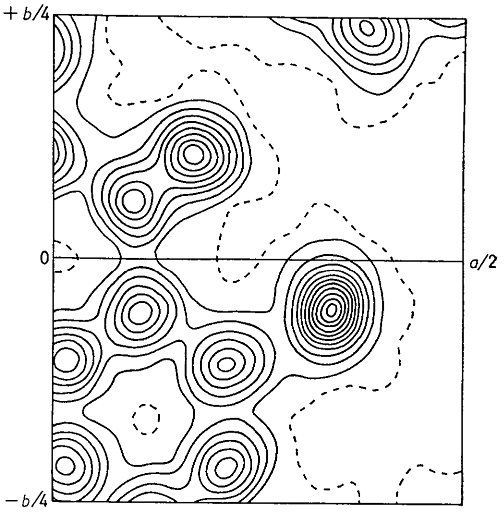

Fig. 2. Final Fourier projection on (001).

carried out by difference syntheses. The first of these (Fig. 3(a)) showed very clearly an asymmetrical vibration of the chlorine atom, there being two positive peaks, one on either side of the chlorine position and approximately in the direction of the b axis, and two negative peaks at right-angles in the direction of the a axis. Since the vibration directions in projection correspond quite closely with the crystallographic axes, and β is very nearly 90°, the asymmetry can be expressed by the factor

$$\exp(-B_1h^2a^{*2}/4\lambda^2)\exp(-B_2k^2b^{*2}/4\lambda^2)\ ,$$

where B_1 and B_2 correspond to the [a] and [b] directions respectively. Approximate values of B_1 and B_2 were obtained by plotting $\log(F_o/F_c)$ against h^2a^{*2} for constant k, and against k^2b^{*2} for constant h.

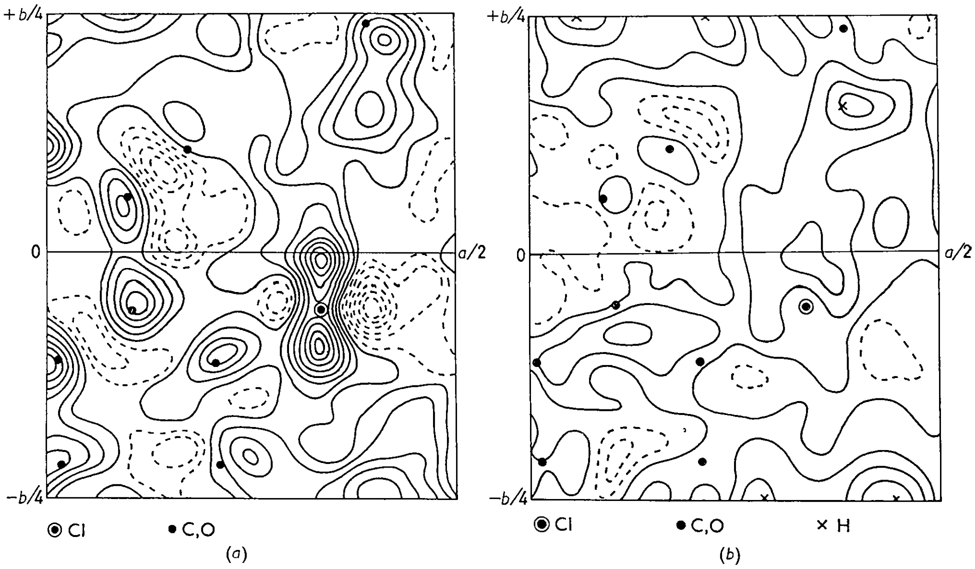

Fig. 3. (a) First and (b) final [c] difference synthesis. Contours at 0·2 e.Å^{-2}.

A total of six difference syntheses were then carried out during which, in addition to refinement of the coordinates, the values of B_1 and B_2 were adjusted to 4·0 Å^2 and 7·5 Å^2 respectively, and the average temperature factor of 5·8 Å^2, determined for the whole molecule, was replaced by 4·8 Å^2 for C_1, C_4 and C_7; 5·5 Å^2 for C_2 and C_3; 3·8 Å^2 for C_5 and C_6; and 6·5 Å^2 for O_8 (see Fig. 5 for nomenclature). An F_c synthesis was used to correct the coordinates for termination of series. In the final difference synthesis (Fig. 3(*b*)) all the atomic centres lie at almost zero electron density, and the gradient, if any, is too slight to warrant further correction. Three positive peaks occur where the hydrogen atoms are to be expected. The R factor, with no allowance for hydrogen contributions, has a value of 0·107.

A [*b*] Patterson projection was unhelpful in determining the inclination of the molecule from the (001) plane. Trial z coordinates were chosen from consideration of the strongest planes and the projected bond lengths, and were such that, whilst keeping the molecule more or less planar, the resulting bond lengths did not vary considerably from normal values. The *h*0*l* structure-factor agreement was good, but little refinement was obtained from [*b*] Fourier projections because of the overlap occurring. The z coordinates were refined by successive three-dimensional syntheses along lines parallel to the c axis and through the final x and y coordinates. A termination-of-series correction was determined by an F_c synthesis.

The incorporation into the *hk*0 structure factors of different temperature factors for the individual atoms and an anisotropic factor for the chlorine atom has not been carried out in the three-dimensional calculations. Average values of B of 4·4 and 3·0 Å^2 were obtained for the *hk*1 and *hk*2 zones respectively by plotting $\log (F_o/F_c)$ against $4 \sin^2 \theta$. The values of R are 0·192 and 0·251 for these zones.

The final atomic coordinates are listed in Table 1.

Table 1. *Fractional atomic coordinates*

Atom	x/a	y/b	z/c
C_1	0·2096	0·8903	0·238
C_2	0·2123	0·7864	0·214
C_3	0·1117	0·7348	0·089
C_4	0·0143	0·7864	0·959
C_5	0·0108	0·8916	0·986
C_6	0·1082	0·9483	0·128
C_7	0·0952	0·0565	0·117
O_8	0·1745	0·1086	0·333
Cl_9	0·3381	0·9471	0·425

Observed and calculated structure factors are compared in Tables 2, 3 and 4 for the *hk*0, *hk*1, and *hk*2 reflections.

Table 2. *Comparison of observed and calculated F*(*hk*0)*'s*

h k	0	1	2	3	4	5	6	7	8	9	10	11	12	13	14
0			25.8 -22.6		29.6 -25.9		36.2 +36.7		< 1.3 + 0.6		4.2 + 5.0		6.6 + 7.9		1.3 - 0.8
1		35.7 +39.8	8.1 + 7.6	26.0 +22.6	14.4 +15.7	3.5 - 2.7	9.0 + 9.8	16.3 -16.6	10.8 -12.0	20.8 +22.0	12.4 +12.4	3.4 + 3.6	2.7 + 3.4	5.4 - 5.1	1.3 - 1.2
2	30.5 +34.8	32.6 +33.2	19.2 -16.8	11.1 - 9.2	38.0 -36.6	2.0 - 1.4	15.0 +13.6	9.4 + 8.6	5.3 - 6.5	5.6 + 5.8	5.2 - 6.8	1.5 - 0.1	7.1 + 7.4	< 0.9 + 1.6	1.8 - 1.6
3		25.8 -24.9	59.5 -67.1	19.7 +19.6	33.3 +32.1	40.9 -38.8	8.1 + 5.4	9.0 - 8.4	14.9 -14.4	8.3 + 7.4	10.0 + 9.7	< 1.3 - 0.9	1.5 + 1.6	4.5 - 3.9	2.4 - 4.1
4	4.4 + 0.2	27.0 +24.7	7.6 + 9.8	10.7 + 9.0	15.5 -16.2	28.6 -27.5	9.3 - 8.7	6.9 + 7.8	5.2 + 4.6	5.7 + 5.2	2.3 - 1.6	6.3 - 6.9	1.2 + 0.2	1.7 + 2.8	
5		16.7 -13.8	17.4 -15.1	15.2 +13.6	17.6 +19.3	3.3 - 4.0	2.7 - 1.0	1.6 - 0.1	12.2 -14.0	< 1.4 - 1.4	8.1 + 9.4	2.3 - 2.0	2.9 + 3.7	< 0.7 + 0.5	
6	57.7 -54.2	32.3 +31.8	5.2 + 4.2	2.5 - 2.6	9.5 + 9.2	21.5 -21.6	9.8 - 8.8	14.4 +14.2	< 1.4 - 1.2	4.3 + 5.4	2.8 + 2.5	6.3 - 5.8	2.0 - 2.2	1.9 + 2.6	
7		8.8 - 6.2	13.3 -13.8	14.2 -15.8	4.7 + 4.7	1.4 + 1.6	1.5 - 1.5	7.6 + 7.3	4.3 - 4.2	9.8 -10.2	1.3 + 0.3	< 1.2 - 0.7	< 0.8 + 0.7		
8	11.3 -11.4	6.2 + 6.0	1.7 + 1.2	7.4 + 7.8	12.9 +14.4	15.4 -14.7	< 1.4 - 2.2	< 1.4 - 0.3	< 1.4 + 1.0	< 1.3 - 0.1	1.9 + 3.1	5.0 - 4.3	2.9 - 3.3		
9		12.4 +11.3	2.0 + 1.4	10.3 -10.3	1.3 + 2.8	26.7 +26.0	3.9 - 3.8	6.7 + 6.6	< 1.4 - 2.0	6.3 - 5.8	1.0 0.0	< 0.8 + 0.6	0.7 + 0.4		
10	4.4 - 4.8	< 1.3 - 0.1	< 1.3 + 1.5	2.6 - 3.0	19.6 +18.4	6.1 + 6.1	4.0 + 2.2	2.4 + 0.8	< 1.3 0.0	< 1.2 - 0.2	2.3 + 2.7	2.0 + 1.9			
11		1.7 + 1.0	2.3 + 3.4	6.8 - 6.7	< 1.4 - 2.2	3.9 + 4.2	6.1 + 4.7	3.8 + 4.0	< 1.2 + 1.0	4.0 - 4.6	1.6 + 0.9				
12	11.0 -13.3	3.6 - 3.4	1.4 + 1.2	1.7 + 1.2	< 1.4 0.0	5.7 + 5.3	3.5 - 3.6	4.3 - 3.1	1.1 - 0.3	< 0.8 - 0.3	0.7 - 1.0				
13		3.8 - 4.0	2.4 + 2.7	< 1.3 + 0.5	< 1.3 - 1.5	< 1.2 - 0.6	2.1 - 1.0	< 0.9 + 0.2	1.2 + 1.8	1.6 - 2.5					
14	1.8 - 2.2	3.8 - 4.3	< 1.2 + 0.6	< 1.2 - 1.3	< 1.2 0.0	2.6 + 3.0	1.9 - 1.0	< 0.7 - 0.3	< 0.3 0.0						
15		< 1.1 0.0	2.0 + 1.7	< 0.9 - 0.1	1.7 - 2.0	4.0 - 2.9	< 0.6 + 0.6								
16	< 0.8 + 0.7	< 0.8 - 1.2	< 0.8 - 0.4	< 0.7 + 0.1	2.6 - 2.6										

Table 3. *Comparison of observed and calculated F(hkl)'s*

k \ h	13	12	11	10	9	8	7	6	5	4	3	2	1	0	$\bar{1}$	$\bar{2}$	$\bar{3}$	$\bar{4}$	$\bar{5}$	$\bar{6}$	$\bar{7}$	$\bar{8}$	$\bar{9}$	$\bar{10}$	$\bar{11}$	$\bar{12}$	$\bar{13}$
0		13		13		40		37		33		20				82		15		18		3		19		< 2	
		-10		+11		+37		-34		+33		+16				+102		+15		-16		- 2		+19		- 2	
1	< 2	< 2	6	2	4	9	12	6	30	6	35	13	15	22	81	53	11	7	9	4	17	8	8	< 2	4	6	5
	+ 2	+ 1	+ 6	+ 2	+ 1	+ 8	+11	- 6	+24	- 6	-27	+16	-16	+23	+101	+58	-11	- 8	-11	+ 5	+22	+ 6	-11	0	+ 3	+ 6	+10
2	3	11	2	7	13	12	16	25	19	9	15	17	30	47	4	4	9	23	12	27	12	5	8	8	10	< 2	2
	- 2	- 7	+ 2	+ 5	+12	+ 6	-12	-19	+14	-11	+15	+13	-24	-48	+10	+ 5	-14	+25	+13	-26	+11	- 4	-10	+ 6	-11	- 1	+ 2
3	< 2	< 2	3	12	12	20	10	4	3	28	67	31	14	6	3	20	13	24	17	6	?	14	4	3	< 2	< 2	3
	- 2	0	+ 3	-11	-10	+16	+ 7	+ 5	- 2	-24	-56	+25	+12	- 7	+ 2	+29	-13	-29	-13	- 6	1	+14	- 5	- 3	- 1	- 2	+ 3
4	6	3	7	< 2	4	4	18	< 2	7	30	27	7	34	7	10	9	17	8	20	13	13	4	9	4	8	< 2	< 2
	- 1	- 2	+ 5	0	+ 4	+ 6	-15	+ 3	+ 6	-27	+23	+ 5	-33	+10	-10	-12	-20	+ 8	+22	-12	-13	- 5	-10	+ 6	+ 9	- 1	0
5	< 2	< 2	< 2	9	6	13	6	6	4	35	3	25	17	23	21	41	6	2	11	17	5	9	< 2	< 2	< 2	< 2	< 2
	+ 1	+ 1	0	- 6	- 4	+10	+ 3	+ 3	- 1	-26	- 2	+22	+19	+23	-23	+44	- 6	- 2	+12	-18	- 6	+ 9	- 1	0	0	- 2	- 1
6	1	4	7	4	< 2	13	14	11	24	5	3	2	30	6	16	26	3	< 2	14	6	6	< 2	3	6	6	< 2	< 2
	- 4	+ 4	+ 6	- 4	+ 1	-12	-13	+ 9	+21	- 6	- 2	- 2	-30	- 3	-19	-26	- 3	- 2	+16	+ 7	- 7	0	- 3	- 6	+ 7	0	- 1
7		< 2	2	9	< 2	3	7	8	9	16	10	4	< 2	9	31	5	4	2	< 2	12	3	4	4	< 2	2	5	
		+ 1	- 2	- 7	+ 2	+ 3	- 6	+ 8	-11	-16	+11	+ 2	- 1	+ 9	-30	+10	+ 8	- 2	- 4	-15	- 7	+ 8	+ 5	0	- 1	- 5	
8		4	4	< 2	5	10	6	10	< 2	13	5	11	7	13	10	< 2	4	14	6	14	14	6	< 2	6	< 2	< 2	
		+ 4	+ 3	- 2	- 3	- 7	- 6	+ 6	- 1	+10	+ 6	-12	- 8	+17	-12	+ 3	- 3	-19	+ 8	+13	-14	+ 6	- 1	- 6	0	+ 2	
9				< 2	10	< 2	8	< 2	5	5	41	6	7	3	3	< 2	8	3	12	5	5	< 2	< 2	< 2			
				- 1	+10	0	- 6	- 2	+ 1	- 4	+42	+ 6	- 9	+ 3	- 7	+ 2	+11	+ 3	+11	- 4	+ 1	- 1	+ 5	0			
10				< 2	< 2	3	< 2	5	4	21	4	< 2	< 2	7	2	4	< 2	6	< 2	17	8	3	< 2	4			
				- 1	- 2	- 5	+ 1	+ 7	+ 2	+13	- 3	- 6	+ 2	+12	+ 4	+ 4	+ 1	-12	- 4	+19	+ 8	+ 4	0	- 5			
11				3	< 2	< 2	4	< 2	6	9	11	5	< 2	< 2	8	< 2	3	< 2	< 2	9	< 2	< 2	< 2	< 2			
				+ 3	+ 3	- 1	- 3	- 1	- 6	+ 8	+11	- 5	- 1	- 2	+13	- 2	+ 6	- 1	- 1	+ 9	- 4	- 1	+ 4	0			
12						5	< 2	< 2	6	6	< 2	< 2	8	< 2	4	6	3	3	< 2	< 2	2	< 2					
						- 6	+ 3	+ 5	- 7	- 6	0	- 5	+11	+ 2	+ 8	- 6	+ 4	- 5	- 1	+ 2	+ 3	+ 2					
13							< 2	< 2	< 2	< 2	< 2	< 2	< 2	3	7	5	< 2	< 2	< 2	< 2	2						
							- 1	- 1	- 2	+ 6	+ 2	- 2	+ 1	- 5	-10	-10	+ 1	+ 3	+ 2	+ 4	- 3						
14							3	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2						
							+ 5	+ 1	- 3	- 1	- 3	0	+ 5	+ 1	+ 3	- 2	+ 2	+ 1	- 5	+ 1	+ 3						
15										< 2	5	< 2	< 2	< 2	< 2	< 2	< 2	< 2									
										+ 5	- 5	- 5	+ 1	- 2	+ 2	- 5	- 1	+ 2									
16													< 2	< 2	< 2												
													+ 4	- 2	+ 1												

Description of the structure

The mean plane of the molecule is inclined at 28° to the *ab* plane, the arrangement in this plane being shown in Fig. 4. There are no intermolecular forces other than those of the van der Waals type, and intermolecular approaches of less than 4·0 Å are shown in this figure. In addition there are contacts between adjacent layers of molecules along the *c* axis, which are separated by a perpendicular distance of 3·45 Å.

The interatomic distances and interbond angles are given in Fig. 5. Of particular interest in this structure are the distortions from planarity of the molecule, which occur in order to give sufficient distance between the chlorine atoms and the quinonoid oxygen

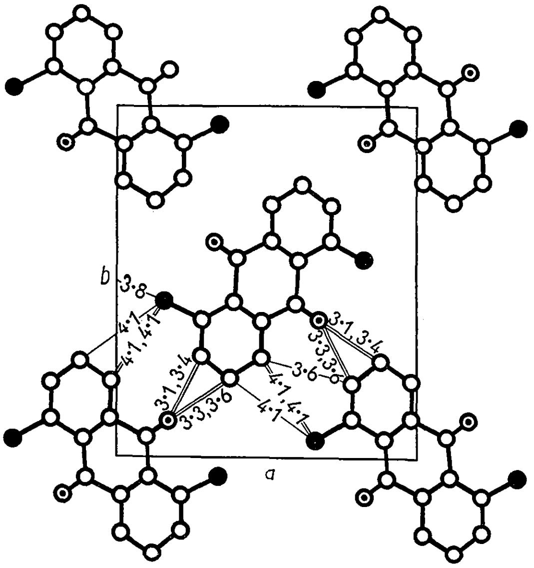

Fig. 4. Arrangement of molecules in the unit cell.

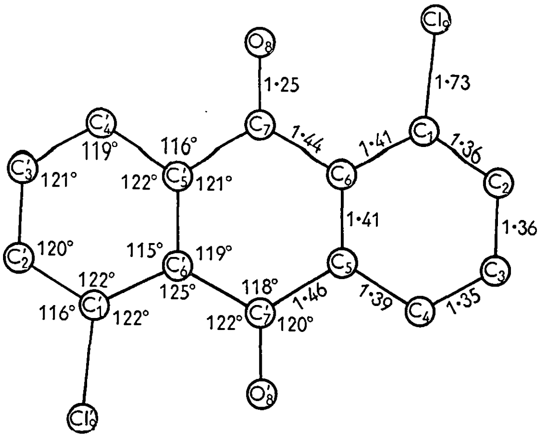

Fig. 5. Dimensions of the molecule.

Table 4. *Comparison of obserwed and calculated $F(hk2)$'s*

k \ h	12	11	10	9	8	7	6	5	4	3	2	1	0	$\bar{1}$	$\bar{2}$	$\bar{3}$	$\bar{4}$	$\bar{5}$	$\bar{6}$	$\bar{7}$	$\bar{8}$	$\bar{9}$	$\overline{10}$	$\overline{11}$	$\overline{12}$	$\overline{13}$
0	10		7		8		37		3		13				47		6		7		6		8		7	
	+8		+5		+10		+32		+3		−11				+60		−6		+6		+7		−8		+7	
1	< 2	17	5	18	7	26	12	27	10	24	8	8	< 4	19	8	34	23	14	3	17	6	< 4	< 4	9	8	< 2
	+1	−11	+5	+13	+5	+23	−11	−24	+8	+24	−9	+9	+8	−30	+8	+44	+21	+17	+1	−18	+5	+3	−3	+10	+9	−6
2	3	5	3	9	16	22	22	6	2	16	31	12	8	4	3	30	5	13	5	5	< 4	13	9	< 3	3	5
	−2	−3	−4	−5	−14	+14	+13	−1	+3	−17	−33	+17	+5	−4	+1	+41	−8	−21	+5	+4	+4	+16	−15	−6	+2	+5
3	2	11	10	9	7	3	8	9	21	16	5	11	17	12	15	3	< 3	7	8	19	7	< 4	< 3	< 3	6	
	−2	−9	+5	+5	−7	−3	−2	−6	+19	−14	−4	−8	−15	−13	−12	+3	−4	+6	+7	−18	−13	+1	−3	+3	+6	
4	< 2	4	< 3	13	11	23	11	8	< 3	21	22	32	12	2	8	21	13	14	3	10	8	5	< 3	5	< 2	
	−2	−3	+1	−9	−5	+18	+8	−7	+2	−20	−29	+38	+12	+3	+11	+26	−16	−18	+1	−99	−3	+8	−4	−6	+2	
5	6	3	16	3	8	12	18	11	21	3	4	8	16	7	14	12	12	< 3	12	< 4	15	4	< 3	< 3	7	
	−5	+2	+12	−2	−3	−7	−18	+9	+19	−1	+3	−6	−17	+11	−19	−12	+10	−2	+14	+6	−18	−5	−3	−2	+11	
6		5	< 3	7	6	13	13	4	< 3	12	7	11	3	3	20	14	< 3	8	< 4	< 4	< 4	4	< 3	< 3	3	
		−4	+2	−5	−5	+10	−12	−4	+2	−9	+5	+11	−3	+7	−20	+16	0	−9	0	−2	−2	+7	+2	−2	−3	
7		6	9	6	9	15	11	9	16	11	< 3	2	16	8	16	16	8	8	11	7	11	4	3	4		
		+4	+7	−6	−5	−9	−8	+8	+15	−14	+1	−1	−22	+10	−20	−15	−5	−9	+15	+7	−15	+2	−1	−5		
8			< 2	< 3	12	4	16	9	< 4	4	26	18	7	5	8	7	8	< 4	< 4	8	5	6	6			
			−1	−3	+11	+4	−10	−6	+7	−4	+29	+17	−8	+3	−8	−3	+14	0	−9	−9	−2	−4	+11			
9			3	6	< 3	< 3	< 3	< 4	< 4	19	3	12	4	10	< 4	< 4	< 4	4	3	9	5	< 3	< 2			
			+3	−6	0	+2	−3	+7	−1	+9	+3	+6	+1	+14	−4	−4	+1	−6	+3	+21	−4	−1	−1			
10				4	11	< 3	10	< 3	< 4	< 4	29	8	5	3	4	< 4	7	< 3	6	7	4	4	< 2			
				+2	+11	−1	−10	+3	−1	+1	+35	−8	−10	−3	−5	+1	+13	+3	0	−4	0	−1	+7			
11				3	4	< 3	2	3	< 4	6	4	< 3	< 4	4	5	7	4	3	< 3	5	9	< 2				
				−4	+4	−3	+3	+6	−4	−8	−7	0	+8	+10	−3	−7	+3	−7	−1	+7	−5	+1				
12					2	< 2	7	< 3	< 3	< 3	< 3	< 3	< 3	< 3	9	< 3	< 3	< 3	< 3	< 2	< 2					
					−1	−4	−7	0	−3	+3	+3	−6	−2	−3	−10	−3	+5	+5	−4	+2	−2					
13							6	< 3	7	< 3	< 3	< 3	6	< 3	< 3	7	< 3	< 2	< 2	< 2						
							+6	+5	−10	−3	+1	−2	+9	+2	+5	−8	−2	−1	−7	+4						
14								+ 4	< 2	< 2	< 2	6	< 3	< 3	< 3	6	< 2	< 2								
								+3	+2	+5	−2	−10	+1	0	0	−11	−2	+5								
15											< 2	< 2	< 2	< 2	< 2	< 2										
											+3	−2	−3	0	+5	+1										

atoms. This is brought about in two ways: (i) a slight buckling into a chair-shape of the central ring; and (ii) an increase in the relevant interbond angles from 120°. The angles C_7–C_6–C_1, O_8–C_7–C_6 and C_6–C_1–Cl_9 are increased to 125°, 122° and 122° respectively. The interatomic distance of 2·79 Å which is found between O_8 and Cl_9 would in fact have been 2·52 Å in a planar molecule with the same bond lengths, but with the above angles equal to 120°. The oxygen and chlorine atoms lie 0·12 and 0·18 Å respectively from the mean plane through the anthraquinone nucleus, i.e. all atoms except the substituting chlorines. The perpendicular distances of the carbon atoms out of this plane range from 0·04 to 0·10 Å. It was apparent from these figures that the planarity of the molecule could be more precisely described in terms of the mean plane through the outer rings including the chlorine atoms, i.e. atoms $C_1C_2C_3C_4C_5C_6Cl_9$ and the corresponding centrosymmetrical atoms. This plane has the equation

$$0{\cdot}4146x+0{\cdot}0676y-0{\cdot}9075z = 0$$

referred to the axes a, b and c' (c' is perpendicular to a and b). The perpendicular distances (in Ångström units) of the atoms from this plane are

C_1	C_2	C_3	C_4	C_5
+0·017	+0·023	−0·039	+0·022	+0·003

C_6	C_7	O_8	Cl_9
−0·005	−0·142	−0·287	−0·008

This clearly illustrates the planarity of the outer rings, and the extent of the chair-shaped distortion of the central ring caused by the bonds C_6–C_7, C_5'–C_7, and C_7–O_8 (likewise C_6'–C_7', C_5–C_7', and C_7'–O_8' in the opposite sense) being inclined from the plane defined by the rest of the molecule.

References

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