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The Crystal Structure of 1,5-Dinitro-4,8-dihydroxyanthraquinone

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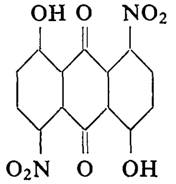
The crystal structure of 1,5-dinitro-4,8-dihydroxyanthraquinone has been determined by X-ray diffraction methods and has been refined using 744 three-dimensional structure amplitudes, giving $R = 8{\cdot}1\%$. The anthraquinone nucleus is approximately planar, but the nitro groups are inclined by about 88° to it. There is the possibility of internal hydrogen bonding, and all the oxygen atoms show large anisotropic thermal vibrations.

Introduction

The crystal structure determination of 1,5-dinitro-4,8-dihydroxyanthraquinone



was undertaken as part of an investigation of the distortions from planarity of substituted anthraquinone molecules. The first structure in this series to be studied was that of 1,5-dichloroanthraquinone (Bailey, 1958), in which small distortions from planarity occur in the central ring, while the outer rings and chlorine atoms remain planar.

Experimental

The unit-cell dimensions were measured on oscillation, rotation and Weissenberg photographs, the mean values being:

$$a = 10{\cdot}17,\ b = 10{\cdot}49,\ c = 6{\cdot}015\ \text{Å},\ \beta = 94°34'.$$

The space group is $P2_1/a$ with two centrosymmetric molecules per unit cell. The experimental specific gravity determined by flotation in sodium iodide solution was 1·697, while that required by the X-ray data is 1·715.

Intensity data were obtained from Weissenberg photographs about **a** (zero layer only) and **c** (zero and four layers). A long and a short exposure using three superposed films were taken for each setting, and the intensities of the spots were estimated by comparison with a calibrated scale of timed exposures from the same crystal.

Structure determination

Correlation of the spacings of strong $\{hk0\}$ reflexions with repeat distances in the molecule enabled the orientation of the rings in the **c** direction to be determined, but did not distinguish between three possible trial structures at 60° to each other. A sharpened Patterson [*c*] projection was computed in which the terms were modified by $1/f_c^2$. This was interpreted and preliminary atomic coordinates determined although no distinction was made between the –OH and –NO_2 groups. However, these were clearly identifiable after

Table 1. *Atomic parameters*

The expression for the thermal ellipsoid used in the structure amplitude calculations includes the term $\exp\left[-\frac{1}{4}(h^2a^{*2}B_{11} + 2hka^*b^*B_{12} + \ldots)\right]$.

	x/a	y/b	z/c	B_{11}	B_{22}	B_{33}	B_{12}	B_{23}	B_{13}
C(1)	0·1565	0·1297	−0·2910	3·56	3·00	3·68	0·02	0·01	1·20
C(2)	0·1632	0·2612	−0·2974	4·71	2·78	4·14	0·36	−0·39	1·57
C(3)	0·0920	0·3320	−0·1629	5·19	2·94	5·18	0·12	−0·45	2·04
C(4)	0·0129	0·2710	−0·0163	5·06	2·54	4·21	−0·16	0·02	1·77
C(5)	0·0062	0·1392	−0·0092	4·45	2·83	3·39	−0·03	−0·23	1·25
C(6)	0·0808	0·0649	−0·1507	3·81	2·68	3·66	−0·12	−0·44	0·99
C(7)	0·0753	−0·0751	−0·1449	4·70	3·05	3·57	−0·39	0·09	1·64
N	0·2383	0·0645	−0·4485	4·02	3·22	4·29	0·33	0·28	1·25
O(1)	−0·0550	0·3453	0·1139	7·82	2·72	5·83	−0·39	0·09	4·16
O(2)	0·1379	−0·1372	−0·2713	9·53	2·87	6·51	−0·80	−0·18	5·81
O(3)	0·1908	0·0434	−0·6301	9·18	8·54	3·16	−3·97	0·74	0·66
O(4)	0·3470	0·0354	−0·3823	3·96	12·96	10·53	−1·73	7·07	0·10
H(1)	−0·1162	0·2980	0·2274	B (isotropic) = 9·50					
H(2)	0·2255	0·3075	−0·4103	= 5·71					
H(3)	0·0961	0·4349	−0·1687	= 4·53					

Table 2. *Observed and calculated structure amplitudes*

H	K	L	F(OBS)	F(CAL)
2	0	0	14.9	+14.3
4	0	0	19.5	-21.4
6	0	0	10.7	+11.1
10	0	0	4.1	-4.7
12	0	0	7.6	+9.3
1	1	0	34.1	+33.4
2	1	0	13.8	+14.2
3	1	0	14.4	-14.8
4	1	0	17.7	-18.4
5	1	0	9.2	+9.0
6	1	0	4.2	+3.8
7	1	0	8.5	-9.2
9	1	0	3.5	+3.7
0	2	0	16.3	+16.7
1	2	0	28.5	+29.2
2	2	0	43.1	-42.3
3	2	0	18.2	-17.8
4	2	0	7.4	-7.6
5	2	0	10.6	+10.9
6	2	0	11.1	-10.1
7	2	0	7.7	+7.9
8	2	0	4.2	-3.8
9	2	0	4.7	+5.3
10	2	0	3.3	-3.4
11	2	0	3.2	-3.4
1	3	0	15.4	+15.1
2	3	0	16.8	-16.7
3	3	0	19.7	+19.8
4	3	0	4.8	-6.4
5	3	0	9.9	-8.5
6	3	0	7.5	+7.6
7	3	0	21.1	-22.7
8	3	0	9.7	-10.4
0	4	0	31.6	-30.7
1	4	0	41.4	+47.4
2	4	0	20.1	-20.5
3	4	0	13.5	-13.9
4	4	0	5.8	+5.4
5	4	0	5.4	-5.1
6	4	0	8.3	+9.3
7	4	0	5.5	-6.2
1	5	0	37.2	-37.1
2	5	0	18.4	+20.3
3	5	0	5.6	+6.0
4	5	0	1.8	-1.8
6	5	0	10.0	+11.2
0	6	0	3.9	-2.6
1	6	0	14.6	+16.6
2	6	0	11.4	+12.1
3	6	0	6.2	-7.3
4	6	0	8.3	-8.4
5	6	0	2.7	-3.3
6	6	0	4.4	+3.8
7	6	0	6.1	-6.3
3	7	0	5.6	-6.3
4	7	0	2.3	+3.1
5	7	0	10.4	+11.3
7	7	0	18.4	+21.6
8	7	0	6.3	-8.1
1	8	0	5.7	+5.5
2	8	0	3.0	+3.6
3	8	0	3.9	+4.1
4	8	0	3.5	-3.8
5	8	0	2.9	+3.2
6	8	0	18.8	+21.4
7	8	0	6.8	+8.8
8	8	0	2.6	+3.1
4	9	0	3.7	-3.9
5	9	0	4.9	-5.1
8	9	0	2.8	+3.8
0	10	0	19.1	-24.2
1	10	0	2.7	-3.1
2	10	0	3.3	-3.7
3	10	0	3.3	+3.4
5	10	0	2.7	-2.7
1	11	0	2.6	-2.5
3	11	0	4.4	+5.0
0	12	0	2.9	+3.0
2	12	0	3.4	+3.0
5	12	0	4.8	-5.5
6	12	0	4.2	-5.3
1	13	0	2.3	-2.7
12	0	-1	3.6	+3.7
10	0	-1	16.0	+15.2
8	0	-1	1.8	-1.7
6	0	-1	5.4	-3.9
4	0	-1	16.8	-16.4
2	0	-1	29.9	+28.8
0	0	1	15.3	+19.3
2	0	1	181.9	+179.5
4	0	1	41.3	+41.9
6	0	1	11.1	-10.4
8	0	1	4.0	-3.9
10	0	1	4.0	+3.8
12	1	-1	5.8	-6.8
11	1	-1	7.9	+8.9
9	1	-1	6.1	-5.7
8	1	-1	2.6	-1.9
7	1	-1	12.1	+11.2
5	1	-1	7.7	+5.4
4	1	-1	2.2	+1.2
3	1	-1	10.6	-9.5
2	1	-1	20.0	+18.0
1	1	-1	18.7	-18.4
0	1	1	11.2	-14.3
1	1	1	37.9	+39.9
2	1	1	9.1	+8.6
3	1	1	27.3	+26.5
4	1	1	14.4	+13.1
5	1	1	18.2	-17.9
6	1	1	11.3	-10.6
7	1	1	6.0	+5.2
8	1	1	1.8	+0.7
10	1	1	3.3	+2.9
11	1	1	2.6	-2.8
9	2	-1	5.4	+5.3
8	2	-1	3.6	+3.7
7	2	-1	3.4	-4.0
6	2	-1	13.8	-12.9
5	2	-1	13.9	-13.5
4	2	-1	41.9	-43.5
3	2	-1	40.0	-40.0
2	2	-1	40.0	+41.6
1	2	-1	36.1	+37.8
0	2	1	49.1	-53.5
1	2	1	17.0	-17.6
2	2	1	27.2	-27.8
3	2	1	1.1	-0.8
4	2	1	11.0	+10.1
6	2	1	7.7	-6.9
7	2	1	4.6	+3.9
8	2	1	14.7	-13.9
10	2	1	1.8	+1.7
11	2	1	2.6	+2.6
10	3	-1	3.9	+3.7
8	3	-1	8.1	-7.6
6	3	-1	19.7	+18.7
5	3	-1	38.7	-36.3
4	3	-1	1.3	-1.4
3	3	-1	21.1	-19.3
2	3	-1	6.7	-3.9
1	3	-1	25.7	+24.5
0	3	1	18.7	+18.7
1	3	1	19.4	+18.1
2	3	1	1.6	-1.8
3	3	1	14.0	+12.7
4	3	1	1.4	-1.2
5	3	1	2.2	+1.8
6	3	1	6.5	-6.0
7	3	1	6.4	-5.1
8	3	1	1.9	-0.4
9	3	1	7.1	-6.3
12	4	-1	2.3	-3.3
11	4	-1	4.1	-4.5
8	4	-1	7.5	+8.0
6	4	-1	5.4	-5.6
5	4	-1	14.1	+14.1
4	4	-1	2.8	+1.6
3	4	-1	12.1	-11.5
2	4	-1	30.9	+31.6
1	4	-1	35.1	+35.0
0	4	1	25.4	-24.8
1	4	1	30.1	-29.2
2	4	1	41.2	-40.6
3	4	1	11.0	+9.4
4	4	1	2.6	+2.4
5	4	1	4.0	+3.4
6	4	1	1.6	+1.5
9	4	1	6.8	-5.9
11	5	-1	5.5	-5.2
10	5	-1	4.7	+4.7
9	5	-1	2.8	-2.2
8	5	-1	7.9	-8.1
4	5	-1	5.7	-5.5
3	5	-1	3.7	+3.3
2	5	-1	7.2	-6.7
1	5	-1	2.2	+1.9
0	5	1	22.1	-21.4
1	5	1	38.5	-34.9
2	5	1	1.9	-1.4
3	5	1	25.9	-22.9
4	5	1	14.9	+13.6
5	5	1	2.1	+2.8
6	5	1	2.7	-2.4
8	5	1	3.4	+3.4
10	6	-1	4.8	-5.0
8	6	-1	3.6	+3.8
7	6	-1	4.8	+5.0
6	6	-1	2.8	-2.3
5	6	-1	13.7	+12.6
3	6	-1	7.7	-6.7
2	6	-1	5.7	-5.3
1	6	-1	20.1	+19.6
0	6	1	11.7	+10.6
1	6	1	8.6	-8.4
2	6	1	9.2	-7.2
3	6	1	6.0	-4.2
4	6	1	10.5	+9.9
5	6	1	2.5	+2.4
6	6	1	4.4	-3.3
7	6	1	2.6	+1.6
9	6	1	7.0	-6.1
10	6	1	2.1	+1.7
7	7	-1	2.8	+2.0
6	7	-1	13.2	+13.1
5	7	-1	35.2	+35.1
4	7	-1	2.6	+2.1
3	7	-1	17.3	+16.4
2	7	-1	5.6	-6.1
1	7	-1	12.8	-11.4
0	7	1	4.1	+3.5
1	7	1	3.5	+1.9
2	7	1	1.8	-1.6
5	7	1	2.3	-1.6
6	7	1	3.7	+3.3
7	7	1	10.5	+8.9
9	7	1	10.4	+9.6
10	7	1	2.1	-2.6
6	8	-1	7.5	+6.5
5	8	-1	11.3	-11.0
4	8	-1	29.4	+29.2
3	8	-1	12.3	-11.8
2	8	-1	7.1	-7.9
0	8	1	4.2	+4.7
1	8	1	2.7	-2.3
2	8	1	2.1	+2.3
3	8	1	1.8	-1.3
5	8	1	5.3	+5.0
7	8	1	2.9	+2.1
8	8	1	12.4	+12.1
9	8	1	3.4	+3.2
8	9	-1	2.3	+2.5
7	9	-1	5.7	-5.5
6	9	-1	4.2	-4.0
3	9	-1	6.4	-5.1
2	9	-1	3.7	+3.6
1	9	-1	2.6	-2.4
0	9	1	2.6	+1.4
1	9	1	1.9	-0.6
3	9	1	2.3	-2.5
6	9	1	2.6	-2.4
7	9	1	1.6	-1.8
8	10	-1	2.3	+1.4
7	10	-1	5.3	+4.8
1	10	-1	2.3	-1.9
0	10	1	5.3	-4.4
1	10	1	4.0	+3.0
2	10	1	19.0	-19.2
3	10	1	4.1	-4.0
4	10	1	3.2	-3.5
5	10	1	3.7	+3.3
7	10	1	1.8	-1.9
7	11	-1	2.7	-2.5
6	11	-1	3.3	-3.0
5	11	-1	2.8	-2.3
4	11	-1	1.5	-1.3
3	11	-1	2.2	+2.6
2	11	-1	2.9	-3.2
1	11	-1	4.7	+4.8
1	11	1	1.6	-2.0
3	11	1	2.5	-2.0
5	11	1	2.9	+2.8
6	12	-1	4.0	-4.3
5	12	-1	2.1	-1.5
4	12	-1	8.5	-6.4
3	12	-1	7.0	+7.1
2	12	-1	1.4	-0.7
0	12	1	3.5	+3.2
2	12	1	3.5	+3.2
3	12	1	1.3	-1.2
1	13	1	2.6	-2.6
12	0	-2	1.2	-0.5
10	0	-2	12.8	+12.9
8	0	-2	16.7	+15.3
6	0	-2	14.9	-15.5
4	0	-2	29.1	+28.3
2	0	-2	39.7	-36.1
0	0	2	13.1	-14.9
2	0	2	69.7	+68.0
4	0	2	57.2	+60.9
6	0	2	6.5	+4.6
8	0	2	5.7	+5.0
10	0	2	1.8	-1.6
12	1	-2	1.4	-1.6
10	1	-2	13.3	-14.5
9	1	-2	17.5	+17.7
8	1	-2	3.5	-3.6
7	1	-2	5.5	-4.4
5	1	-2	2.3	+2.1
4	1	-2	6.1	-4.4
3	1	-2	21.4	+19.3
2	1	-2	5.8	+5.4
1	1	-2	3.0	-3.2
0	1	2	14.1	+15.5
1	1	2	14.9	-14.4
2	1	2	11.3	-10.7
3	1	2	16.8	+16.2
4	1	2	7.4	+7.1
5	1	2	14.9	+13.9
6	1	2	8.4	+7.4
8	1	2	3.5	-2.7
9	1	2	3.7	-3.8
12	2	-2	1.6	+1.9
8	2	-2	5.1	-4.6
7	2	-2	5.7	+6.0
5	2	-2	7.7	-7.2
4	2	-2	6.2	+7.0
3	2	-2	6.5	-6.9
2	2	-2	53.7	-60.8
1	2	-2	34.1	-35.5
0	2	2	4.9	+4.6
1	2	2	4.7	+5.1
2	2	2	6.2	+6.4
3	2	2	4.2	+4.1
4	2	2	22.1	-21.5
6	2	2	3.4	-3.4
7	2	2	4.2	-4.2
8	2	2	3.5	+3.1
9	2	2	1.8	+2.0
10	2	2	6.8	-6.6
12	3	-2	1.4	+1.4
11	3	-2	3.3	-3.8
10	3	-2	5.4	-4.8
9	3	-2	1.8	+1.8
8	3	-2	6.1	+5.9
7	3	-2	3.7	+3.4
6	3	-2	2.2	-2.5
5	3	-2	13.0	-12.5
4	3	-2	12.7	+11.2
3	3	-2	46.2	-47.9
1	3	-2	13.8	-13.0
1	3	2	17.6	+17.2
2	3	2	7.1	+7.4
3	3	2	5.4	+4.6
4	3	2	2.0	-2.2
5	3	2	6.8	+5.8
6	3	2	1.6	-0.9
7	3	2	2.7	+2.7
9	3	2	7.0	-6.2
10	3	2	2.5	-2.7
11	4	-2	1.9	-2.0
10	4	-2	3.4	-3.1
9	4	-2	4.7	-5.2
8	4	-2	2.2	-2.1
7	4	-2	3.0	-2.5
6	4	-2	8.6	+8.3
5	4	-2	7.5	-6.9
4	4	-2	8.1	+8.6
3	4	-2	29.6	+29.2
2	4	-2	3.0	-2.9
1	4	-2	7.5	-7.7
0	4	2	11.6	+10.5
1	4	2	2.1	+2.2
3	4	2	1.9	+2.6
4	4	2	22.5	-21.0
5	4	2	5.3	+3.5
6	4	2	4.4	-4.0
7	4	2	2.6	-2.5
8	4	2	4.1	+3.8
9	4	2	3.4	+3.1
10	5	-2	2.0	-1.8
9	5	-2	10.0	-9.9
8	5	-2	11.6	+11.1
6	5	-2	7.7	-7.0
4	5	-2	13.7	-14.2
3	5	-2	5.1	-4.6
1	5	-2	7.1	+5.7
0	5	2	2.9	-2.3
1	5	2	2.6	+2.4
2	5	2	13.5	-14.0
3	5	2	26.4	-25.2
5	5	2	11.4	-10.5
6	5	2	2.5	+2.1
7	5	2	2.0	+2.2
8	5	2	3.3	+2.5
9	5	2	1.9	-0.6
11	6	-2	2.5	+2.9
9	6	-2	3.3	+3.6
8	6	-2	8.9	-9.1
3	6	-2	23.6	+23.3
2	6	-2	1.5	-1.5
1	6	-2	4.6	-4.4
0	6	2	7.8	-6.8
1	6	2	1.5	+1.6
2	6	2	8.5	+7.2
3	6	2	6.5	+6.2
4	6	2	5.7	-4.5
5	6	2	4.9	-4.5
7	6	2	2.7	-2.0
9	6	2	3.5	+3.4
5	7	-2	10.2	+9.5
4	7	-2	12.6	+12.0
3	7	-2	37.5	+38.8
2	7	-2	3.3	+3.0
1	7	-2	16.9	+15.4
0	7	2	5.7	-5.2
1	7	2	6.5	-5.4
2	7	2	4.1	+2.9
8	7	2	4.9	+4.3
9	7	2	6.4	+6.1
10	8	-2	2.1	+2.1
8	8	-2	2.7	-2.5
7	8	-2	1.8	+1.9
6	8	-2	5.6	-5.3
5	8	-2	5.5	-4.6
4	8	-2	13.7	+12.0
3	8	-2	7.2	-6.7
2	8	-2	29.4	+29.7
1	8	-2	9.8	-9.8
0	8	2	6.9	-7.4
1	8	2	7.7	-7.0
2	8	2	1.9	+1.8
3	8	2	2.8	+2.2
8	8	2	2.1	+1.2
9	9	-2	4.0	-4.6
6	9	-2	3.9	+4.1
5	9	-2	6.0	-5.5
4	9	-2	4.9	-4.6
3	9	-2	4.4	-4.3
1	9	-2	5.0	-5.0
0	9	2	2.6	+2.1
3	9	2	2.3	-2.3
7	9	2	2.1	-2.0
8	10	-2	3.9	-3.7
6	10	-2	3.7	+3.4
5	10	-2	5.5	+5.0
3	10	-2	2.1	+1.9
1	10	2	4.6	-3.5
2	10	2	6.5	-5.6
3	10	2	2.5	+2.2
4	10	2	11.2	-10.8
5	11	-2	2.8	-2.5
4	11	-2	4.1	-3.3
3	11	-2	4.7	-4.1
2	11	-2	1.5	-1.4
1	11	-2	2.9	+2.9
0	11	2	2.6	-2.8
1	11	2	3.5	+3.7
2	11	2	1.5	+1.6
3	11	2	2.3	-1.8
4	11	2	1.5	-1.7
5	12	-2	2.3	-2.7
4	12	-2	7.1	-6.8
2	12	-2	8.6	-6.3
1	12	-2	6.9	+6.8
2	12	2	2.1	+1.7
3	12	2	1.4	+1.5
4	12	2	2.2	+2.6
10	0	-3	2.2	-1.9
8	0	-3	23.2	+23.1
6	0	-3	25.2	+26.3
4	0	-3	28.9	-31.2
2	0	-3	8.4	+10.2
0	0	3	12.5	+13.6
2	0	3	23.9	-27.1
4	0	3	25.6	+26.0
6	0	3	29.9	+34.3
8	0	3	3.2	-2.7
11	1	-3	2.1	+1.7
10	1	-3	2.2	-2.3
8	1	-3	19.6	-21.4
7	1	-3	20.2	+15.8
6	1	-3	10.5	-10.3
5	1	-3	2.5	+1.6
4	1	-3	5.4	+4.4
3	1	-3	5.6	+4.1
2	1	-3	4.1	-2.7
1	1	-3	7.6	+7.5
0	1	3	1.4	+1.3
2	1	3	8.4	+8.2
3	1	3	6.3	-5.6
4	1	3	8.5	-7.6
5	1	3	13.5	+13.4
6	1	3	6.0	+5.8
8	1	3	3.4	+2.7
9	1	3	2.2	+2.3
12	2	-3	2.3	-2.3
11	2	-3	2.2	+2.4
6	2	-3	4.1	+4.3
5	2	-3	10.4	+9.9
4	2	-3	10.7	-9.5
3	2	-3	9.5	-7.6
2	2	-3	11.2	-9.7
1	2	-3	13.9	-14.0
0	2	3	11.9	-11.1
1	2	3	3.0	-2.5
2	2	3	14.1	-13.4
3	2	3	5.3	-4.7
4	2	3	3.0	-3.3
5	2	3	3.2	-2.7
6	2	3	2.3	+1.8
7	2	3	5.4	+4.8
8	2	3	3.5	-3.3
9	2	3	2.0	-2.6
11	3	-3	2.1	+1.9
10	3	-3	5.4	+4.8
9	3	-3	4.3	-4.4
8	3	-3	5.3	-4.2
6	3	-3	5.0	-3.5
5	3	-3	8.5	+7.8
4	3	-3	7.4	+5.3
3	3	-3	14.7	-13.5
2	3	-3	15.2	+13.1
1	3	-3	40.3	-40.1
0	3	3	9.3	-9.4
1	3	3	10.4	-9.3
2	3	3	6.4	+6.4
3	3	3	8.8	+6.9
4	3	3	1.4	+0.3
5	3	3	5.0	+4.5
6	3	3	2.6	+2.0
7	3	3	2.0	-1.7
9	3	3	1.6	+1.6
10	4	-3	3.5	-3.7
9	4	-3	6.4	-6.1
8	4	-3	9.2	-7.8
7	4	-3	6.0	-6.9
6	4	-3	8.6	+8.1
4	4	-3	6.2	+4.5
3	4	-3	8.1	-8.3
1	4	-3	9.5	+9.1
0	4	3	12.8	+13.3
1	4	3	11.7	+11.7
2	4	3	1.3	-1.0
3	4	3	6.5	-6.1
4	4	3	5.7	-5.1
5	4	3	3.6	-2.7
6	4	3	3.6	-3.2
7	4	3	6.2	+6.5
8	4	3	2.1	-1.9
10	5	-3	4.7	+4.8
9	5	-3	2.1	-1.6
8	5	-3	1.6	+2.0
7	5	-3	14.2	-13.9
6	5	-3	10.2	+8.6
5	5	-3	3.3	-1.4
4	5	-3	5.1	-3.3
3	5	-3	2.9	+1.9
2	5	-3	10.3	-9.9
1	5	-3	1.4	-0.8
0	5	3	6.1	-5.3
2	5	3	2.7	+2.1
4	5	3	6.9	-6.8
5	5	3	11.7	-11.7
6	5	3	2.6	+2.4
7	5	3	5.6	-5.2
8	5	3	2.0	-2.1
9	6	-3	2.7	+2.1
8	6	-3	2.3	-2.1
7	6	-3	3.2	+3.5
6	6	-3	6.8	-6.3
5	6	-3	3.7	+3.5
4	6	-3	6.1	-3.8
3	6	-3	2.2	-2.6
2	6	-3	3.2	-2.0
1	6	-3	9.3	+8.5
0	6	3	3.5	+2.6
1	6	3	6.4	+6.4
2	6	3	2.9	-1.2
6	6	3	2.5	-2.4
9	7	-3	3.9	+3.6
6	7	-3	3.4	-3.8
5	7	-3	3.5	-3.0
4	7	-3	3.5	+3.9
3	7	-3	14.9	+13.8
2	7	-3	12.8	+12.6
1	7	-3	36.1	+37.3
1	7	3	8.6	+6.8
2	7	3	3.7	-3.1
9	8	-3	1.5	-1.4
8	8	-3	2.5	+2.5
6	8	-3	2.0	-2.0
5	8	-3	6.9	+6.3
4	8	-3	7.8	-6.7
3	8	-3	5.8	-5.1
2	8	-3	15.9	+13.7
1	8	-3	9.7	-8.7
0	8	3	21.8	+21.1
2	8	3	2.3	-2.2
3	8	3	4.9	-5.0
8	9	-3	5.3	-5.4
7	9	-3	5.1	-4.2
6	9	-3	3.5	-2.8
5	9	-3	3.9	-4.0
4	9	-3	4.4	+4.5
3	9	-3	5.5	-4.7
2	9	-3	4.8	-4.5
1	9	-3	2.3	-2.0
0	9	3	2.8	+2.1
1	9	3	6.3	-5.8
5	9	3	3.0	-2.8
7	10	-3	2.1	-2.0
6	10	-3	4.4	-3.7
5	10	-3	2.9	+2.2
4	10	-3	5.3	+4.6
3	10	-3	5.1	+4.6
3	10	3	2.8	-2.5
4	10	3	4.4	-4.1
6	10	3	4.9	-5.8
3	11	-3	2.3	-2.2
2	11	-3	3.9	-3.4
1	11	-3	3.5	-2.8
3	11	3	2.6	+2.3
3	12	-3	3.4	-3.7
2	12	-3	6.8	-6.6
0	12	3	6.4	-5.5
1	12	3	6.5	+4.8
6	0	-4	25.6	+26.7
4	0	-4	17.3	+19.1
2	0	-4	3.5	-4.3
0	0	4	10.7	-10.9
2	0	4	6.5	+5.8
6	0	4	6.1	+5.6
8	0	4	9.8	+12.8
11	1	-4	4.8	-5.0
8	1	-4	5.6	-5.1
7	1	-4	8.6	+8.6
6	1	-4	18.9	-22.7
5	1	-4	14.5	+14.2
4	1	-4	8.9	-9.2
3	1	-4	3.4	-2.8
2	1	-4	1.6	-1.6

Table 2 (*cont.*)

H	K	L	F(OBS)	F(CAL)
1	1	-4	7.2	+9.0
1	1	4	2.8	-3.0
3	1	4	4.0	+4.2
4	1	4	2.9	+2.6
5	1	4	5.1	-5.0
6	1	4	5.1	-5.0
7	1	4	8.2	+8.6
8	1	4	2.8	+3.5
11	2	-4	2.2	-1.9
10	2	-4	2.8	-2.5
9	2	-4	6.5	+6.0
7	2	-4	2.8	+3.4
6	2	-4	5.4	-5.9
3	2	-4	4.2	+4.4
2	2	-4	8.2	+8.9
1	2	-4	1.8	+1.3
0	2	4	18.0	-21.8
1	2	4	10.2	-11.3
2	2	4	7.8	-7.9
4	2	4	3.0	+3.3
6	2	4	5.8	-6.1
7	2	4	3.3	-3.4
8	2	4	1.8	+0.7
9	2	4	2.2	+2.3
11	3	-4	2.3	-1.8
10	3	-4	1.8	-1.0
9	3	-4	1.8	+1.4
8	3	-4	4.0	+3.2
7	3	-4	3.9	-3.5
4	3	-4	4.7	-3.8
3	3	-4	5.7	+5.4
2	3	-4	2.8	-3.2
1	3	-4	9.3	-9.3
0	3	4	13.1	+14.2
1	3	4	20.3	-22.3
2	3	4	7.7	-7.9
3	3	4	2.7	-2.0
4	3	4	4.6	+4.1
6	3	4	3.3	-2.4
7	3	4	2.3	+2.2
8	3	4	1.5	+1.9
10	4	-4	2.6	+2.3
8	4	-4	2.2	-2.7
7	4	-4	8.1	-7.5
6	4	-4	13.4	-14.3
5	4	-4	6.1	-7.6
4	4	-4	5.8	+6.0
3	4	-4	5.1	-3.7
2	4	-4	12.1	+12.3
1	4	-4	7.1	+5.8
0	4	4	5.1	-4.7
1	4	4	2.8	-2.6
2	4	4	4.0	+3.9
4	4	4	4.1	+3.6
6	4	4	4.2	-3.8
7	4	4	2.8	-3.4
8	4	4	2.3	-2.2
9	4	4	1.9	+2.4
10	5	-4	3.5	-3.6
8	5	-4	2.1	+1.2
7	5	-4	5.8	-4.6
6	5	-4	7.4	+8.1
5	5	-4	11.9	-12.8
4	5	-4	9.8	+9.6
3	5	-4	1.4	+0.4
2	5	-4	8.2	-8.4
1	5	-4	3.6	-3.0
1	5	4	2.9	+2.1
2	5	4	5.8	-4.9
4	5	4	3.3	+2.8
5	5	4	2.1	-1.7
6	5	4	3.2	-3.7
7	5	4	4.9	-5.5
9	6	-4	1.5	-1.7
8	6	-4	4.8	+4.2
7	6	-4	4.1	+4.2
6	6	-4	6.4	-5.4
5	6	-4	2.5	+2.0
4	6	-4	6.8	-6.6
3	6	-4	2.3	-1.6
2	6	-4	1.5	+0.6
1	6	-4	9.0	+8.6
3	6	4	2.5	-1.3
4	6	4	2.3	+1.9
5	6	4	3.7	+4.1
8	6	4	2.1	-2.7
9	7	-4	2.3	-3.1
8	7	-4	2.2	-1.9
7	7	-4	2.9	+2.4
6	7	-4	1.4	+1.9
5	7	-4	2.3	+2.0
4	7	-4	3.2	-3.6
2	7	-4	2.3	+1.9
1	7	-4	7.9	+7.0
0	7	4	10.0	+10.7
1	7	4	23.8	+26.6
2	7	4	3.6	-2.7
3	7	4	4.6	+4.1
7	8	-4	1.4	+1.4
4	8	-4	2.6	-2.7
3	8	-4	2.6	+2.5
2	8	-4	5.6	-5.0
0	8	4	12.3	+13.0
1	8	4	5.5	-5.8
2	8	4	11.3	+11.1
6	9	-4	6.1	-5.9
5	9	-4	3.9	-3.2
4	9	-4	2.9	-2.3
3	9	-4	2.5	-2.4
2	9	-4	2.7	+2.8
1	9	-4	6.2	-6.2
0	9	4	4.1	-4.3
2	9	4	2.3	+2.5
3	9	4	3.4	-3.3
6	10	-4	5.1	-5.7
5	10	-4	3.7	-3.6
4	10	-4	3.4	-3.3
3	10	-4	2.1	+1.5
2	10	-4	3.4	+2.8
1	10	-4	4.2	+4.8
1	11	-4	3.2	-2.7
0	11	4	3.5	-3.1

the first [*c*] electron density projection. Three refinement cycles were calculated, after which the overall temperature factor ($B=4\cdot38$), and absolute scale factor were determined by plotting $\log(F_o/F_c)$ against $4\sin^2\theta$. After applying these values, two [*c*] difference projections were calculated, from which it was evident that B for the oxygen atoms was considerably higher than for the carbon atoms. The overall value of B was therefore replaced by values of 3·0 for carbon, 4·5 for nitrogen and 6·5 for the oxygen atoms. The value of the residual R was in this way reduced to 14·9% for the $F(hk0)$ terms.

Trial z coordinates were obtained by assuming that the molecule would lie in the (201) plane, which gave by far the strongest reflexion on the photographs. Four successive [*a*] electron density projections were calculated in order to refine the z coordinates, but there was considerable overlapping of some of the atoms, and the accuracy was not as high as in the refinement of the [*c*] projection.

When the Ferranti Pegasus computer became available, six further cycles of least-squares refinement were carried out, and with isotropic temperature factors only, the value of R for all $F(hkl)$ was 22·0%. After an interval of several years the refinement was continued, using anisotropic temperature factors for all the atoms; this caused R to fall rapidly to 8·1%, when the shifts in the parameters indicated were less than the standard deviations. During the refinement, hydrogen atoms were included at their calculated positions assuming C–H and O–H = 1·08 Å, but only their isotropic thermal parameters were refined. A total of 744 structure amplitudes were used, and the mean standard deviation for the coordinates was 0·005 Å.

The final values of the atomic coordinates and anisotropic temperature factors are listed in Table 1, and the observed and calculated structure amplitudes are compared in Table 2.

Description of the structure

The structure consists of discrete molecules with no bonding forces, other than van der Waals, between them. The bond lengths and inter-bond angles derived from the final set of atomic coordinates are listed in Table 3, and shown diagrammatically in Fig. 1 together with the numbering of the atoms. The values of the dimensions of the molecule agree well with those found in other similar structure determinations.

Table 3. *Bond lengths and inter-bond angles*

C(1)–C(2)	1·383 Å	C(1)–C(2)–C(3)	120·1°
C(2)–C(3)	1·351	C(2)–C(3)–C(4)	119·3
C(3)–C(4)	1·395	C(3)–C(4)–C(5)	120·7
C(4)–C(5)	1·385	C(4)–C(5)–C(6)	120·0
C(5)–C(6)	1·418	C(5)–C(6)–C(1)	116·9
C(6)–C(1)	1·368	C(6)–C(1)–C(2)	123·0
C(6)–C(7)	1·470	C(5)–C(6)–C(7)	120·8
C(7)–C(5′)	1·456	C(1)–C(6)–C(7)	122·3
C(1)–N	1·477	C(6)–C(5)–C(7′)	119·2
N——O(3)	1·180	C(4)–C(5)–C(7′)	120·8
N——O(4)	1·185	C(6)–C(7)–C(5′)	120·0
C(4)–O(1)	1·336	C(6)–C(7)–O(2)	119·8
C(7)–O(2)	1·219	O(2)–C(7)–C(5′)	120·2
		C(3)–C(4)–O(1)	117·0
		C(5)–C(4)–O(1)	122·4
		C(2)–C(1)–N	114·4
		C(6)–C(1)–N	122·6
		C(1)–N——O(3)	118·1
		C(1)–N——O(4)	117·5
		O(3)–N——O(4)	124·4

Mean standard deviation for bonds 0·005 Å
Mean standard deviation for angles 0·6°

The geometry of the molecule was considered in detail by calculating the equations of the planes containing (*a*) the central ring of the anthraquinone nucleus, (*b*) one of the outer rings, and (*c*) the nitro group. That of the central ring which includes the origin of the unit cell is

$$0\cdot7156\,X-0\cdot0084\,Y+0\cdot6985\,Z=0$$

where X, Y and Z are standard orthogonal coordinates defined by $X=x+z\cos\beta$, $Y=y$, and $Z=z\sin\beta$. The distances of the atoms out of this plane are C(5) −0·0026, C(6) +0·0026, and C(7) −0·0025 Å. The extra-ring atom O(2) is displaced from this plane by −0·0272 Å.

The equation of the mean plane through one of the outer rings of the anthraquinone nucleus is

$$0\cdot7114\,X-0\cdot0143\,Y+0\cdot7027\,Z=0\cdot0122$$

from which the perpendicular distances of the atoms are C(1) −0·0020, C(2) +0·0016, C(3) −0·0033, C(4) +0·0019, C(5) +0·0005 and C(6) +0·0032 Å. The extra-ring atoms N and O(1) are displaced by −0·0108 and +0·0034 Å respectively out of this plane. The anthraquinone nucleus may therefore be regarded as planar within experimental error, since the outer and central rings are inclined to each other by only 0·4°.

The equation of the plane of the nitro group is

$$0{\cdot}3649\,X + 0{\cdot}8774\,Y - 0{\cdot}3115\,Z = -2{\cdot}3941$$

from which plane atom C(1) is displaced by +0·0254 Å. This plane of the nitro group makes an angle of 88·4° with the plane of the outer ring and 87·9° with the central ring of the anthraquinone nucleus. This twisting is in order to allow adequate clearance between the quinone oxygen O(2) and the nitro group oxygen

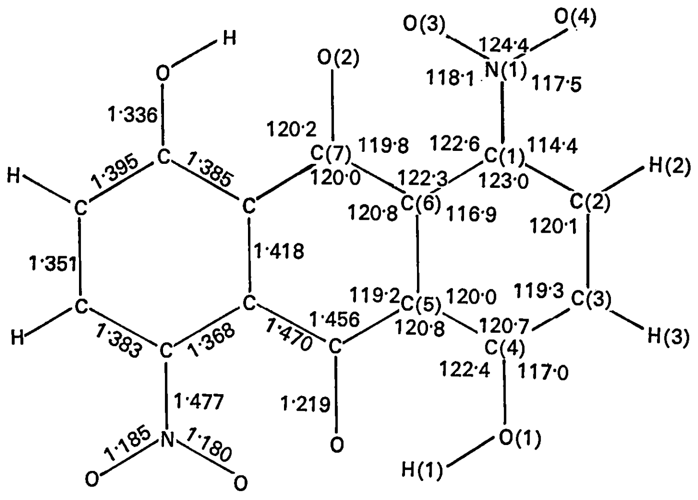


Fig. 1. Bond lengths and inter-bond angles.

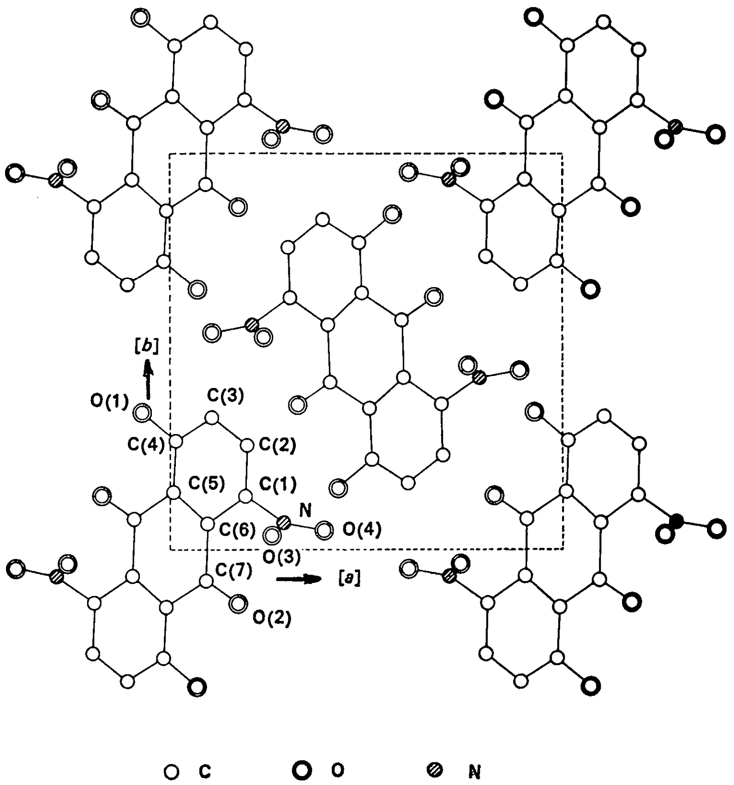


Fig. 2. Diagrammatic [c] projection, showing packing of the molecules in the unit cell.

atoms O(3) and O(4), these distances being only 2·953 and 2·911 Å respectively.

The only short distance of approach between non-bonded atoms in the molecule is O(1) to O(2′) = 2·549 Å. This may result in an internal hydrogen bond, but as the position of H(1) has not been determined experimentally, this can not yet be regarded as confirmed.

Fig. 2 shows the packing of the molecules in the unit cell.

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Crystallographic Studies of Metal–Peptide Complexes.
IV. (Glycyl-L-histidinato)copper(II) Sesquihydrate

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(Glycyl-L-histidinato)copper(II) sesquihydrate crystallizes from solution at *p*H 6·5. The blue crystals are tetragonal, space-group $P4_32_12$, with $a = 11{\cdot}24 \pm 0{\cdot}02$, $c = 17{\cdot}84 \pm 0{\cdot}04$ Å, $Z = 8$. The copper atom has coordination number 5. The four closest donor atoms, which have an approximately square arrangement abou the copper, are the amino-, peptide- and imidazole-1- nitrogen atoms of one peptide molecule and a carboxyl oxygen atom of another. The fifth donor atom, completing a square-pyramidal arrangement, is the oxygen of a water molecule. The copper also interacts weakly with the second oxygen atom of the carboxyl group to which it is bonded. The additional semi-molecule of water indicated by the composition of the complex lies on a twofold axis and participates in the hydrogen-bond network. The structure was refined by full-matrix anisotropic least squares, the final reliability index *R* being 0·086 for the 1341 independent observed reflexions.

Introduction

This structure analysis is the fourth of a series‡ dealing with model compounds for metal–protein interaction (Freeman, Robinson & Schoone, 1964; Freeman, Schoone & Sime, 1965; Freeman & Taylor, 1965). The potential usefulness of structural information about this particular complex was suggested to us by the demonstration that, in solution, sperm-whale metmyoglobin binds copper(II) ion at the imidazole groups of histidine residues (Breslow & Gurd, 1963). This conclusion has already been supported by a study of the 1:1 Cu^{II}-metmyoglobin complex in the solid state (Banaszak, Kendrew & Watson, 1965). We therefore set out to make a detailed study of histidine–Cu^{II} interaction in a much simpler system. Preliminary accounts of this work (Blount, Fraser, Freeman, Szymanski, Wang & Gurd, 1966) and of the closely related structure of (β-alanyl-L-histidinato)copper(II) dihydrate (Freeman & Szymanski, 1965) have been published.

Experimental

The complex was prepared from a solution of glycyl-L-histidine hydrochloride (0·001 mole) in 0·2*M* sodium hydroxide (5–6 ml). Freshly precipitated and washed copper(II) hydroxide (0·0015 mole) was added. The resulting violet solution was centrifuged, separated from undissolved copper hydroxide, and carefully titrated with 0·15*M* hydrochloric acid until the colour was blue (*p*H 6·5). Blue crystals separated overnight. The specimen used to record the crystallographic data had a square-pyramidal shape with curved faces.

Crystal data

$C_8H_{10}O_3N_4Cu \, . \, 1\tfrac{1}{2}H_2O$ F.W. 300·8.

Tetragonal, $a = 11{\cdot}24 \pm 0{\cdot}02$, $c = 17{\cdot}84 \pm 0{\cdot}04$ Å, $D_m = 1{\cdot}72 \pm 0{\cdot}02$, $D_x = 1{\cdot}772$ g.cm^{-3}, $U = 2253{\cdot}9$ Å^3, $Z = 8$, $F(000) = 1208$. $\lambda(\text{Cu } K\alpha_1) = 1{\cdot}5405$ Å, $\lambda(\text{Cu } K\alpha_2) = 1{\cdot}5443$ Å.

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‡ The crystals were grown by H.C.F. while a guest at the University of Indiana, Indianapolis. The data were recorded and the intensities were measured in Sydney by J.T.S. and C.-H.W. respectively. The structure was solved independently by J.F.B. and K.A.F. in Sydney, and by C.-H.W. in Tokyo with the help of Dr Y. Saito. This paper is based on the Sydney refinement calculations.