

## Short Communications

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**The crystal structure of juglone:** By P. D. CRADWICK\* and D. HALL,† *Chemistry Department, University of Alberta, Edmonton, Alberta, Canada*

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The crystal structure of juglone (5-hydroxy-1,4-naphthaquinone) has been solved, using three-dimensional photographic data. The crystals are monoclinic,  $a=7.34$ ,  $b=7.69$ ,  $c=13.91$  Å,  $\beta=99.2^\circ$ , space group  $P2_1/n$ . The packing arrangement is very similar to that for naphthazarin (formally 5,8-dihydroxy-1,4-naphthaquinone), in spite of the difference of the one hydroxyl, and as a consequence the structure is disordered.

As part of an investigation of the crystal structures of hydroxyl-substituted naphthaquinones, the crystal structure of juglone (5-hydroxy-1,4-naphthaquinone) has been determined.

## Experimental

Commercially available juglone was recrystallized from acetone to give orange needles elongated on  $a$ . The crystals are monoclinic,  $a=7.34 \pm 0.02$ ,  $b=7.69 \pm 0.02$ ,  $c=13.91 \pm 0.03$  Å,  $\beta=99.2 \pm 0.1^\circ$ ;  $D_m$ , by flotation in aqueous zinc bromide,  $1.47$  g.cm $^{-3}$ ;  $D_c$ , for 4 molecules per unit cell,  $1.47$  g.cm $^{-3}$ .

Reflexions on even layers about  $a$  were normal, but those on odd layers were weak and very diffuse, so much so that intensity measurement was difficult for the first layer and not possible for the third. Intensities were measured visually from Weissenberg photographs of the zero, first, second and fourth layers, taken with Cu  $K\alpha$  radiation. The crystal used was a needle of hexagonal section, maximum dimension 0.01 cm, and no absorption corrections were considered necessary. The  $h0l$  data were also collected, but

because of the unsuitable crystal shape were used only for initial scaling of the  $a$ -axis layers.

Systematic absences are in  $h0l$  with  $h+l$  odd, and  $0k0$  with  $k$  odd, and the space group is thus  $P2_1/n$ . If however the weak reflexions are ignored and the strong reflexions indexed on the basis of  $a=3.67$  Å, the absence in  $h0l$  is for  $l$  odd, and the apparent space group is  $P2_1/c$ , with 2 molecules per sub-cell. The structure then approximates one in which a molecule is centred on the origin of  $P2_1/c$ , *i.e.* in the true space group  $P2_1/n$  an approximately centrosymmetric molecule must be centred at  $\frac{1}{2}, 0, 0$ . The weak reflexions correspond to the deviation from actual centrosymmetry, and the fact that these are diffuse indicates that the structure is partly disordered with respect to the pseudo-centrosymmetry.

The orientation of the naphthalene skeleton was readily established from the Patterson function. Initially three-quarter-weight atoms were assumed at all four possible oxygen positions, and this centrosymmetric molecule was refined in  $P2_1/c$ . The experimentally determined scale factors were assumed initially, but thereafter the scale factor for each layer was treated as a variable. Scattering factors were as in *International Tables for X-ray Crystallography* (1969). Block-diagonal least-squares refinement reduced  $R$  from an initial 0.49 to 0.26. At this point one of the two oxygen atoms had a much higher temperature factor than the

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Table 1. *Thermal parameters* (Å $^2$ )

The temperature factor is of the form

$$\exp \{-2\pi^2(U_{11}h^2a^*2 \dots + 2U_{12}hka^*b^* \dots)\}.$$

Atom	$U_{11}$	$U_{22}$	$U_{33}$	$U_{12}$	$U_{13}$	$U_{23}$
C(1)	0.04 (2)	0.038 (9)	0.067 (12)	0.01 (1)	-0.01 (1)	0.022 (7)
C(2)	0.15 (4)	0.017 (7)	0.078 (12)	0.00 (1)	-0.01 (2)	-0.001 (8)
C(3)	0.07 (4)	0.082 (11)	0.057 (10)	0.03 (2)	0.00 (1)	-0.011 (10)
C(4)	0.04 (2)	0.086 (12)	0.039 (8)	0.02 (1)	-0.02 (1)	0.010 (8)
C(5)	0.09 (3)	0.032 (8)	0.052 (9)	0.00 (1)	0.03 (2)	0.010 (7)
C(6)	0.06 (3)	0.046 (9)	0.067 (11)	0.00 (1)	0.02 (1)	-0.018 (8)
C(7)	0.09 (3)	0.051 (10)	0.044 (9)	-0.02 (1)	-0.01 (1)	-0.033 (7)
C(8)	Isotropic $B=4.2$ (4)					
C(9)	0.07 (3)	0.036 (9)	0.029 (7)	0.02 (1)	0.00 (1)	0.003 (5)
C(10)	0.08 (3)	0.021 (7)	0.035 (8)	-0.01 (1)	-0.01 (1)	0.004 (6)
O(4)	0.10 (2)	0.103 (8)	0.029 (5)	0.021 (9)	-0.012 (8)	0.034 (5)
O(1)	0.14 (3)	0.061 (8)	0.095 (9)	-0.01 (1)	0.00 (1)	0.040 (7)
O(3)	0.17 (3)	0.050 (7)	0.080 (9)	0.01 (1)	0.05 (1)	0.025 (6)

other, and an electron-density synthesis confirmed that the peak height for the former was approximately half that of other atoms. These atoms were given half and full weight respectively, and  $R$  then decreased to 0.23. At this stage the  $1kl$  data were introduced, and the refinement continued in  $P2_1/n$ , i.e. the molecule was no longer assumed to be centrosymmetric and three normal oxygen atoms were assumed. The  $1kl$  data were scaled so that  $\sum F_o = \sum F_c$  for these data. The  $F_o$  values thus obtained were somewhat greater relative to those with  $h$  even than was observed experimentally, and it was assumed that, in effect, this compensated for the diffuseness, and hence apparent low intensity, of the  $1kl$  spots, i.e. that the  $1kl$  data so scaled would more or less be those corresponding to a non-disordered structure. Initially the  $R$  index for the  $1kl$  data was 0.80. Several cautious least-squares cycles followed, during which only the scale constant for the first layer and the positional parameters for atoms were permitted to vary. Agreement between observed and calculated  $1kl$  data steadily improved, and subsequently scale factors for all layers and isotropic temperature factors were also varied. At this stage full-matrix refinement facilities became available, and were used hereafter. The function minimized was  $\sum w(\Delta F)^2$ , where  $w = a^2/[a^2 + (F - b)^2]$ . Parameters  $a$  and  $b$  were varied such that  $\langle w(\Delta F)^2 \rangle$  was invariant with  $F$ ,

the final values being  $a = 6.0$ ,  $b = 4.0$ . The isotropic refinement converged at  $R = 0.17$ . Thereafter scale factors were held constant, and anisotropic thermal parameters permitted. It was never supposed that these would provide complete description of the thermal motion, as the  $U_{11}$  term in particular must be affected by remaining error in the scale factors, but as planar condensed molecules are markedly anisotropic in their vibrations it was thought that the positional parameters so obtained would be more accurate. The justification of this was that the dimensions of the resultant molecule, Fig. 1, are very much as would be expected for 5-hydroxy-1,4-naphthaquinone, and that the agreement between  $F_o$  and  $F_c$  show a marked improvement. At convergence the overall  $R$  was 0.11, and  $R$  values for individual layers were  $0kl$ , 0.10;  $1kl$ , 0.10;  $2kl$ , 0.11;  $4kl$ , 0.15. The apparent thermal parameters are listed in Table 1; some appear to be improbable as such, and indeed the refined parameters for C(8) failed a test to determine definite thermal parameters and an isotropic temperature factor was retained for this atom. The least-squares errors shown on Fig. 1 must certainly be minimal estimates.

A difference synthesis calculated at the conclusion of refinement showed no density feature, positive or negative, greater than  $0.3 \text{ e.}\text{\AA}^{-3}$ . Appropriate peaks could have been

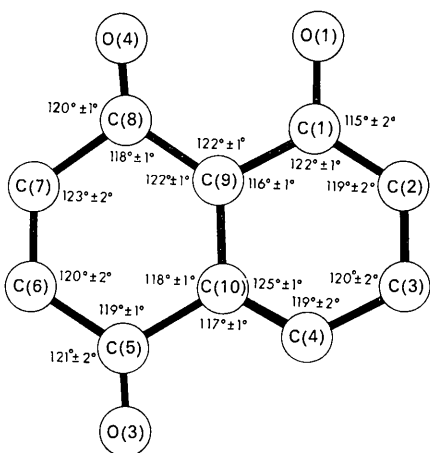
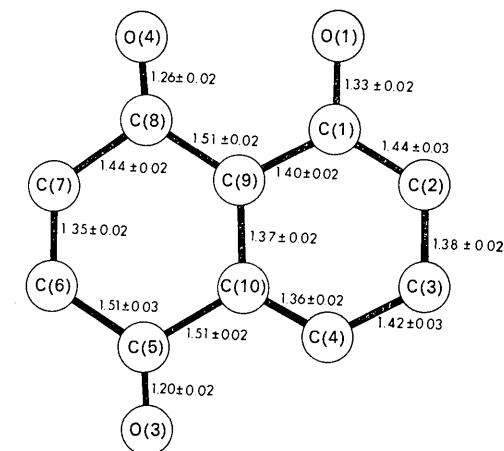


Fig. 1. Bond lengths and angles.

Table 2. Atomic coordinates

Atom	$x/a$	$y/b$	$z/c$
C(1)	0.317 (4)	0.218 (2)	-0.006 (1)
C(2)	0.393 (5)	0.268 (2)	0.090 (1)
C(3)	0.392 (4)	0.149 (3)	0.165 (1)
C(4)	0.310 (4)	-0.016 (2)	0.145 (1)
C(5)	0.172 (4)	-0.239 (2)	0.034 (1)
C(6)	0.098 (4)	-0.291 (2)	-0.067 (1)
C(7)	0.110 (4)	-0.178 (2)	-0.140 (1)
C(8)	0.184 (4)	-0.005 (2)	-0.127 (1)
C(9)	0.253 (3)	0.050 (2)	-0.026 (1)
C(10)	0.254 (3)	-0.061 (2)	0.052 (1)
O(1)	0.336 (3)	0.335 (2)	-0.074 (1)
O(3)	0.166 (3)	-0.337 (2)	0.101 (1)
O(4)	0.185 (2)	0.096 (1)	-0.198 (1)

Table 3. Observed and calculated structure factors ( $\times 10$ )

$k$	$h$	$l$	$F_o$	$F_c$	$k$	$h$	$l$	$F_o$	$F_c$
0	0	0	179	200	0	0	0	179	200
0	0	1	10	10	0	0	1	10	10
0	0	2	17	17	0	0	2	17	17
0	0	3	10	10	0	0	3	10	10
0	0	4	17	17	0	0	4	17	17
0	0	5	10	10	0	0	5	10	10
0	0	6	17	17	0	0	6	17	17
0	0	7	10	10	0	0	7	10	10
0	0	8	17	17	0	0	8	17	17
0	0	9	10	10	0	0	9	10	10
0	0	10	17	17	0	0	10	17	17
0	0	11	10	10	0	0	11	10	10
0	0	12	17	17	0	0	12	17	17
0	0	13	10	10	0	0	13	10	10
0	0	14	17	17	0	0	14	17	17
0	0	15	10	10	0	0	15	10	10
0	0	16	17	17	0	0	16	17	17
0	0	17	10	10	0	0	17	10	10
0	0	18	17	17	0	0	18	17	17
0	0	19	10	10	0	0	19	10	10
0	0	20	17	17	0	0	20	17	17
0	0	21	10	10	0	0	21	10	10
0	0	22	17	17	0	0	22	17	17
0	0	23	10	10	0	0	23	10	10
0	0	24	17	17	0	0	24	17	17
0	0	25	10	10	0	0	25	10	10
0	0	26	17	17	0	0	26	17	17
0	0	27	10	10	0	0	27	10	10
0	0	28	17	17	0	0	28	17	17
0	0	29	10	10	0	0	29	10	10
0	0	30	17	17	0	0	30	17	17
0	0	31	10	10	0	0	31	10	10
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0	0	33	10	10	0	0	33	10	10
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0	0	35	10	10	0	0	35	10	10
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0	0	37	10	10	0	0	37	10	10
0	0	38	17	17	0	0	38	17	17
0	0	39	10	10	0	0	39	10	10
0	0	40	17	17	0	0	40	17	17
0	0	41	10	10	0	0	41	10	10
0	0	42	17	17	0	0	42	17	17
0	0	43	10	10	0	0	43	10	10
0	0	44	17	17	0	0	44	17	17
0	0	45	10	10	0	0	45	10	10
0	0	46	17	17	0	0	46	17	17
0	0	47	10	10	0	0	47	10	10
0	0	48	17	17	0	0	48	17	17
0	0	49	10	10	0	0	49	10	10
0	0	50	17	17	0	0	50	17	17
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0	0	60	17	17	0	0	60	17	17
0	0	61	10	10	0	0	61	10	10
0	0	62	17	17	0	0	62	17	17
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0	0	80	17	17	0	0	80	17	17
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0	0	88	17	17	0	0	88	17	17
0	0	89	10	10	0	0	89	10	10
0	0	90	17	17	0	0	90	17	17
0	0	91	10	10	0	0	91	10	10
0	0	92	17	17	0	0	92	17	17
0	0	93	10	10	0	0	93	10	10
0	0	94	17	17	0	0	94	17	17
0	0	95	10	10	0	0	95	10	10
0	0	96	17	17	0	0	96	17	17
0	0	97	10	10	0	0	97	10	10
0	0	98	17	17	0	0	98	17	17
0	0	99	10	10	0	0	99	10	10
0	0	100	17	17	0	0	100	17	17

interpreted as hydrogen atoms, but others of comparable height could not, and the inclusion of hydrogen atoms was not thought to be justified.

Atom coordinates are listed in Table 2, and observed and calculated structure factors in Table 3. A projection of the structure is shown in Fig. 2 and close intermolecular approaches are listed in Table 4.

Table 4. Close intermolecular contacts

Atom 1	Atom 2	Vector to be applied to atom 2	Distance (Å)
C(2)	O(3)	$x, y+1, z$	3.48
C(2)	O(4)	$\frac{1}{2}+x, \frac{1}{2}-y, \frac{1}{2}+z$	3.51
C(3)	O(4)	$\frac{1}{2}+x, \frac{1}{2}-y, \frac{1}{2}+z$	3.30
C(3)	O(3)	$\frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{2}-z$	3.27
C(7)	O(4)	$\frac{1}{2}-x, \frac{1}{2}+y-1, \frac{1}{2}-z-1$	3.32
O(1)	C(6)	$x, y+1, z$	3.38

### Discussion

The cell parameters for the juglone subcell are very similar to those for modification *A* of naphthazarin (formally 5,8-dihydroxy-1,4-naphthoquinone), and so is the manner of molecular packing. Fig. 2 is virtually identical (other than for the missing oxygen atom) with the corresponding packing diagram for naphthazarin (Fig. 17, Pascard-Billy, 1962); similarly, the angle of inclination of the molecule to *a* is 21.8° for juglone, 23.6° for naphthazarin. The packing mode thus effectively ignores the fact that there is only one hydroxyl group in juglone, and a molecule oriented in the wrong sense, *i.e.*, as if inverted through a centre at the midpoint of the bond C(9)–C(10), could fit without major intermolecular repulsion. The average structure corresponding to such disorder would be a centrosymmetric molecule with half-oxygen atoms attached to C(4) and

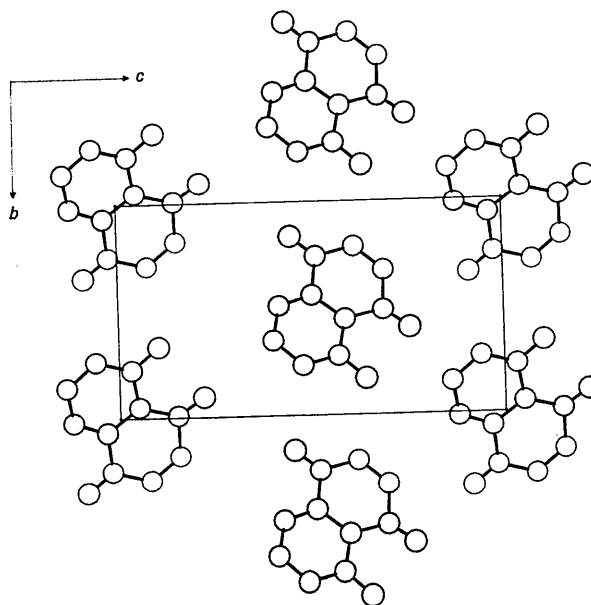


Fig. 2. The structure projected on to (100).

C(8), which was the apparent structure deduced when only the data with *h* even were considered.

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**A method of fitting a plane to a set of points by least squares.** By C. SCHERINGER,\* *Institut für Kristallographie der Technischen Hochschule Aachen, Germany*

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The problem of finding the 'best' plane through a given set of weighted points has been solved in the past by resorting to eigenvalue procedures. It is shown that the solution can be given simply by using standard least-squares routines.

The problem of finding the 'best' plane through a given set of weighted points by least-squares methods has been discussed by Schomaker, Waser, Marsh & Bergman (1959) – hereafter referred to as SWMB. In the treatment given by these authors the plane is introduced in the form of a constraint and the solution is obtained by using the method of Lagrange multipliers. This approach finally involves the determination of the minimum eigenvalue of a  $3 \times 3$  symmetric matrix. Blow (1960) has proposed transforming

the SWMB equations into an orthonormal metric, and Hamilton (1961) has discussed a more general weighting system.

The SWMB treatment may be described as a 'direct' approach to a non-linear least-squares problem, which is solved by means of an eigenvalue determination. On the other hand every least-squares problem can be linearized and solved if approximate solutions, sufficiently close to the correct solution, are known. In the case of the 'best' plane approximate solutions can always be obtained by calculating the position of the plane from three points of the set. Thus it should be possible to find the 'best' plane

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