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)	$x, \quad y+1, \quad z$	3·48
C(2)	O(4)	$\frac{1}{2}+x, \frac{1}{2}-y, \quad \frac{1}{2}+z$	3·51
C(3)	O(4)	$\frac{1}{2}+x, \frac{1}{2}-y, \quad \frac{1}{2}+z$	3·30
C(3)	O(3)	$\frac{1}{2}-x, \frac{1}{2}+y, \quad \frac{1}{2}-z$	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)	$x, \quad y+1, \quad z$	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-naphthaquinone), 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 C(8), which was the apparent structure deduced when only the data with *h* even were considered.

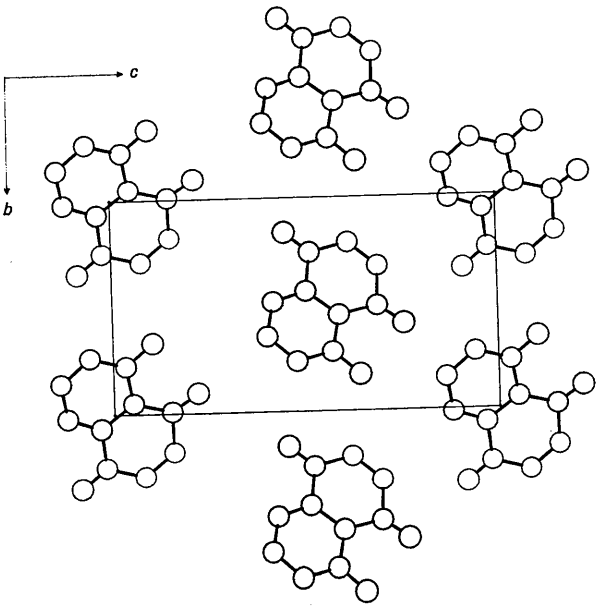

Fig. 2. The structure projected on to (100).

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A method of fitting a plane to a set of points by least squares.

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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 3×3 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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by simply using standard least-squares routines. Such an approach will be described in this paper.

First we show that the 'best' plane passes through the centre of gravity of the set of given points with weights (or 'masses') w_r, $r=1\cdots N$. We choose a Cartesian coordinate system XYZ as reference system in which the points may have the positions $\mathbf{X}_r$. We assume that a 'best' plane in the least-squares sense exists and that its orientation has already been determined. We introduce a second Cartesian coordinate system UVW such that the W axis coincides with the normal of the plane. Then we only have to determine the point on the W axis where it is intersected by the plane. Let this point be described by the parameter W_s, then we have the least-squares condition

$$\sum_r w_r (W_r - W_s)^2 \rightarrow \text{minimum}. \tag{1}$$

Since $\frac{\delta W_r}{\delta W_s}=0$ and $\frac{\delta W_s}{\delta W_s}=1$, the solution of (1) is

$$W_s = \sum_r w_r W_r / \sum_r w_r . \tag{2}$$

Equation (2) means that the 'best' plane cuts the W axis at the W coordinate of the centre of gravity. Since the other two coordinates of the centre of gravity lie somewhere in the plane, we have proved that the plane passes through the centre of gravity.

The second step consists in determining the orientation of the normal of the plane in the reference system. We choose the centre of gravity as origin of both the reference system XYZ and the system UVW. We describe the orientation of the normal of the plane (W axis) by two Eulerian angles; they may be chosen to be θ and ϱ as used by Scheringer (1963) (the third angle φ is set to zero). From Scheringer's (1963) table 1 the transformation of coordinates can be deduced as

$$\left.\begin{aligned} U_r &= X_r\cos\varrho + Y_r\sin\varrho\sin\theta - Z_r\sin\varrho\cos\theta \\ V_r &= \qquad\qquad Y_r\cos\theta + \quad Z_r\sin\theta \\ W_r &= X_r\sin\varrho - Y_r\cos\varrho\sin\theta + Z_r\cos\varrho\cos\theta . \end{aligned}\right\} \tag{3}$$

Now the least-squares condition is

$$Q = \sum_r w_r W_r^2 \rightarrow \text{minimum}, \tag{4}$$

where the W_r are functions of the two parameters θ and ϱ as stated by equations (3). We put $\theta=p_1$, $\varrho=p_2$ and derive from (4)

$$\delta Q/\delta p_j = 2\sum_r w_r W_r\, \delta W_r/\delta p_j = 0\ ,\quad j=1,2\ . \tag{5}$$

There is no direct solution for the two equations (5), and a cyclic procedure, starting with trial values for θ and ϱ, must be used. The elements of the 2×2 matrix of the normal equations are

$$a_{ij} = \sum_r w_r \frac{\delta W_r}{\delta p_i}\cdot\frac{\delta W_r}{\delta p_j}\ , \tag{6}$$

and the right-hand sides are

$$b_j = -\sum_r w_r W_r \frac{\delta W_r}{\delta p_j}\ , \tag{7}$$

from which the shifts for p_1 and p_2 can be calculated. The derivatives $\delta W_r/\delta p_j$ can easily be found from (3).

The equation of the best plane expressed in coordinates of the reference system (origin at centre of gravity) is given by

$$X\sin\varrho - Y\cos\varrho\sin\theta + Z\cos\varrho\cos\theta = 0 \tag{8}$$

with the final values of θ and ϱ. It can be seen from (8) that the relevant range for the two angles is either $0°\le\theta\le 360°$, $0°\le\varrho\le 90°$, or $0°\le\theta\le 180°$, $0°\le\varrho\le 180°$, or some other equivalent. For $\varrho=90°$ a motion in θ only transforms the plane into itself; thus the value of θ is not relevant for this value of ϱ. In actual computations θ should be kept constant for $88°\le\varrho\le 92°$.

Computed refinements showed that the problem is nearly linear in the angle ϱ over a range of about 20°. The same holds for θ when $\varrho=0°$. For larger values of ϱ the linear range in θ decreases because θ becomes less well defined (and undefined for $\varrho=90°$). We used trial values of θ and ϱ which deviated by 10° and 20° from the correct solution for 40 different solution points (θ, ϱ). After one cycle the correct solution for the angle ϱ was obtained within the limits of $\pm 0{\cdot}35°$ and $\pm 1{\cdot}48°$ respectively. The stated limits are average values for the 40 different solution points. The same result holds for θ when $\varrho=0°$. For an average of the ϱ angles in the range $0°\le\varrho\le 80°$ the corresponding error limits for θ are 3·4 and 7·3°. For deviations of more than 40° in θ and ϱ from the correct solution the computed shifts tend to become too large. Therefore we suggest keeping the shifts within the range of $\pm 30°$. With this device proper convergence was always obtained in 5 cycles or less for deviations of 60° from the correct solution in both angles. Even for the maximum possible deviation of 90° proper convergence was obtained in about 80% of the computed cases. In the program, as written for routine use, the following steps are performed:

(1) The atomic parameters are transformed into Cartesian coordinates with the origin at the centre of gravity.
(2) Trial values for the direction cosines of the normal of the plane [coefficients in equation (8)] are calculated from two atoms and the centre of gravity which are non-collinear.
(3) Trial values for the angles θ and ϱ are calculated from the direction cosines.
(4) θ and ϱ are refined in three cycles.

The trial values for θ and ϱ are usually as close as 5° to the correct solution, and thus problems of convergence do not occur.

The problem of determining the 'best' straight line through a set of weighted points allows the same type of solution. The line passes through the centre of gravity. If the direction of the 'best' line is denoted by the W axis, we have by analogy with (4) the least-squares condition

$$\sum_r w_r (U_r^2 + V_r^2) \rightarrow \text{minimum}, \tag{9}$$

where U_r and V_r are functions of the two parameters θ and ϱ as stated by equations (3). The normal equations follow accordingly.

In order to show that the procedure described here gives the same solution as the SWMB treatment we shall express both procedures in terms of the inertial tensor.

We introduce an orthonormal metric in the SWMB equations and obtain for the elements of the matrix $\mathbf{A}$

$$A^{ij} = \sum_r w_r X_r^i X_r^j\ , \tag{10}$$

where $i, j = 1, 2, 3$ denote the three directions of space. The SWMB procedure amounts to finding the minimum eigenvalue of $\mathbf{A}$; its eigenvector points in the direction of the normal of the plane. According to SWMB this eigenvalue

is equal to

$$\lambda_A^{\min} = \sum_r w_r W_r^2 , \quad (11)$$

where the W axis coincides with the normal of the 'best' plane. Since $U_r^2 + V_r^2 + W_r^2 = R_r^2$ is constant for every orientation of the Cartesian system, the relation

$$\mathbf{I} + \mathbf{A} = \mathbf{E} \sum_r w_r R_r^2 \quad (12)$$

is valid, where **I** denotes the inertial tensor and **E** the unit matrix. From (12) it can easily be shown that **I** and **A** are diagonalized by the same transformation, thus we have the analogous relation for the eigenvalues

$$\lambda_I^i + \lambda_A^i = \sum_r w_r R_r^2 , \quad i = 1, 2, 3 . \quad (13)$$

With respect to the procedure described in this paper we first note that equation (4) is equivalent to searching for the maximum possible moment of inertia about the normal of the plane. Thus the normal of the 'best' plane is a principal inertial axis with moment (eigenvalue of the inertial-tensor matrix **I**)

$$\lambda_I^{\max} = \sum w_r (U_r^2 + V_r^2) . \quad (14)$$

However, in the first instance we do not look for this eigenvalue but rather for the corresponding eigenvector, the principal axis of **I**. Then the eigenvalue $\lambda_I^{\max}$ (and hence $\lambda_A^{\min}$) can easily be calculated from equations (3) and (14). (The other two eigenvectors – and eigenvalues – are not determined since they are not relevant.) Thus both approaches give the same result. In principle, the solution described here is of a simpler type; in practice, the differences in computation do not matter when using electronic computers.

Note added in proof: – The program has also been found useful for constructing crystal drawings when used in the following way: The plane of projection has to be defined by three points. The weights of these points must be non-zero, whereas the weights of all other points (atoms) in the unit cell are set to zero. Then the positions of the atoms are given in the final output with in-plane coordinates U and V, and W coordinates normal to the plane. Since the plane of projection is defined by three points in the unit cell, it may not be a lattice plane. In this regard the program is different from that described by Minor & Dyson (1970); see also Buerger (1965).

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A procedure for representing arbitrary phase probability distributions in a simplified form.

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This note presents a least-squares method for fitting the phase probability distributions obtained in protein crystallography by the function $P(\alpha) = \exp(K + A\cos\alpha + B\sin\alpha + C\cos 2\alpha + D\sin 2\alpha)$. The method has been tested with data from crystals of lamprey hemoglobin.

An alternative, and algebraically simplified, representation for the phase probability distributions used in protein crystallography has recently been described (Hendrickson & Lattman, 1970). It adds generality to the treatment of various types of phase information, affords computational advantages over the conventional functional forms and simplifies the combination of phase information from independent sources. It proved to be a convenient and useful aid in the structure analysis of lamprey hemoglobin (Hendrickson & Love, 1971). Unfortunately, the new representation required a reformulation of the error model for the isomorphous replacement method. This revision has been validated by experiment, but it nonetheless renders the new representation incommensurate with the formulations from other error models. Thus, unless computations are begun *de novo*, the advantages of the simplified form are lost to the structure analyses of the many proteins for which phase probability distributions have been computed by other error models. The analysis of such structures might benefit if one could cast the distributions at hand in the alternative representation. In particular, this would facilitate the inclusion of additional phase information, such as from a partial structure or direct methods, in the refinement of atomic models. The close similarity of phase probability curves computed by the usual isomorphous replacement error models with those calculated by the new procedure (Hendrickson & Lattman, 1970) suggests that a good fit by the simplified representation should be possible.

The problem, then, is to find the values of the parameters in the simplified representation,

$$P_c(\alpha) = \exp(K + A\cos\alpha + B\sin\alpha + C\cos 2\alpha + D\sin 2\alpha) , \quad (1)$$

which provide a best fit to an arbitrary 'observed' phase probability distribution, $P_o(\alpha)$. A least-squares minimization of the direct discrepancy between $P_c(\alpha)$ and $P_o(\alpha)$ leads to a set of non-linear normal equations which must be solved by iteration. However, logarithms of the probabi-

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