

## On the Refinement of the Crystal Structures of Phenoquinone and Monoclinic Quinhydrone

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The crystal structures of monoclinic quinhydrone  $C_6H_4O_2 \cdot C_6H_4(OH)_2$  (space group is  $P2_1/c$  with  $a=7.647$ ,  $b=6.001$ ,  $c=11.590$  Å and  $\beta=109^\circ 58'$ ) and phenoquinone  $C_6H_4O_2 \cdot 2(C_6H_5OH)$  (space group is  $P2_1/c$  with  $a=11.152$ ,  $b=5.970$ ,  $c=11.499$  Å and  $\beta=100^\circ 0'$ ) were refined from three-dimensional X-ray diffraction data. Different molecules in each complex are connected by hydrogen bonds between the hydroxyl and the carbonyl group. In quinhydrone, an infinite molecular chain is formed by the hydrogen bonds, while in phenoquinone one quinone molecule is placed between two phenol molecules to form a short complex chain. In spite of this difference between the complex chains, no essential difference was observed between the complexes as regards the short interatomic distances. A significant difference of the C–C–OH bond angles between hydrogen side and the non-hydrogen side was observed.

### Introduction

A systematic investigation of the crystal structure of the molecular complexes between *p*-benzoquinone and hydroxybenzene is going on in the author's laboratory, with special reference to the nature of the charge transfer interaction in these crystals. The structure of triclinic quinhydrone (hereafter called the  $\beta$  form) has already been reported (Sakurai, 1965), and that of the complex between resorcinol and quinone has also been determined (Ito, Minobe & Sakurai, 1966).

Among these complexes, the structure of phenoquinone  $C_6H_4O_2 \cdot 2(C_6H_5OH)$  was studied by Harding & Wallwork (1953), and the monoclinic modification of quinhydrone (hereafter called the  $\alpha$  form) was studied by Matsuda, Osaki & Nitta (1958). Since these two studies were mainly based on two-dimensional data, the structure is reinvestigated by the use of full three-dimensional diffraction data.

### Crystal data

The crystallographic data for  $\alpha$ -quinhydrone given by Matsuda *et. al* are

$$\begin{aligned} a &= 7.647, b = 6.001, c = 11.590 \text{ \AA} \\ \beta &= 109^\circ 58', V = 499.9 \text{ \AA}^3 \\ \text{Space group } &P2_1/c, Z = 2. \end{aligned}$$

The cell dimensions of phenoquinone were redetermined by a Weissenberg camera with a specially designed Straumanis type cassette. These are

$$\begin{aligned} a &= 11.152 \pm 0.004, b = 5.970 \pm 0.004, \\ c &= 11.499 \pm 0.009 \text{ \AA} \\ \beta &= 100.0 \pm 3', V = 754.0 \pm 0.8 \text{ \AA}^3 \\ \text{Space group } &P2_1/c, Z = 2. \end{aligned}$$

### Experimental

Single crystals of quinhydrone, elongated along the *a* axis were obtained from an acetone solution of equal

mol ratios of hydroquinone and *p*-benzoquinone. The zero to 6th layers around the *a* axis and zero to 5th layers around the *b* axis were recorded on multiple film Weissenberg photographs with Cu  $K\alpha$  radiation.

Single crystals of phenoquinone were obtained from a mixture of acetone solutions of 1:2 mol ratio of *p*-benzoquinone and phenol. The zero to 5th layers around the *b* axis and the zero to 7th layers around the [011] axis were recorded.

The densities of the diffracted spots were measured by a Narumi Co. Ltd microphotometer. The observed intensities were corrected for ordinary Lorentz and polarization factors, and reduced to the approximate absolute scale structure amplitudes with the data reduction program RDTR-3 on the HITAC 5020 computer.

### The refinement of the structure

Refinements were started from parameters given by previous authors. The initial *R* indices were 20.4% for quinhydrone and 34.8% for phenoquinone. These parameters were refined in a straightforward way by use of the full-matrix least squares including hydrogen coordinates. Final *R* values for observed reflections are 9.4% for quinhydrone and 10.5% for phenoquinone. Structure factors are shown in Tables 1 and 2, and atomic parameters in Tables 3 and 4.

### Discussion of the structure

#### General description of the crystal structure

Molecular arrangements in the crystals are shown in Fig. 1.

The general structural principle in these compounds is the same as that found in other complexes. Molecules are packed by three kinds of forces in different directions, namely, the hydrogen bond, the charge transfer force and the van der Waals force.

Different molecules in a complex are connected by hydrogen bonds between the hydroxyl group and car-

Table 1. Structure factors for quinhydrone  
The three columns give *l*, *sF*<sub>o</sub>, *F*<sub>c</sub>.

Table with columns representing crystallographic indices (l, s, F) and corresponding structure factor values. The table is organized into multiple columns, with labels like '0 0 L', '1 1 L', '2 2 L', etc., indicating different sets of reflections. The numerical values are arranged in a grid-like format, with some rows and columns containing multiple values for a single index set. The values range from positive to negative integers, often with decimal parts. The table is very dense and covers a wide range of indices, from small integers to larger ones, with some values extending to two decimal places.

Table 2. Structure factors for phenoquinone

The three columns give I, sFo, Fc.

0 0 L	8 2.5 0.7	-3 -32.8 -35.5	10 1 L	9 -19.7 -18.8	-5 -10.8 -9.3
2 26.3 26.5	11 0 L	-2 54.3 59.9	-9 5.7 5.2	10 2.9 3.4	-4 -3.1 -2.7
4 -6.4 -5.2	-10 4.1 4.3	0 24.2 24.1	-7 7.3 6.6	13 2.4 3.3	-3 -3.1 -3.4
6 -18.1 -16.5	-4 -10.1 -10.1	1 -8.2 -5.9	-2 -12.0 -10.0	3 2 L	-2 -3.9 -3.0
8 8.8 8.7	-2 -3.9 -2.7	2 -3.7 -2.3	-1 -6.8 -4.8	-13 8.4 6.7	0 22.4 21.0
12 -13.3 -14.9	2 -2.7 -2.4	3 -16.6 -16.1	0 -4.0 -3.5	-12 -6.3 -4.3	1 4.2 4.7
1 0 L	4 -3.1 -4.9	5 -24.2 -24.0	3 -3.0 -3.1	-11 2.8 2.8	5 2.7 2.6
-14 3.6 4.0	12 0 L	9 11.4 11.9	4 -4.1 -4.7	-8 10.0 8.3	7 4.9 5.1
-10 6.3 6.4	-6 7.1 7.2	10 -16.5 -17.5	5 -2.2 -2.5	-7 -21.2 -19.0	8 -1.9 -2.8
-6 6.3 4.7	0 2.8 1.5	12 -2.9 -3.5	6 -4.0 -4.0	-6 18.0 14.9	10 2 L
-4 -8.0 -6.2	13 0 L	5 1 L	7 -3.2 -1.2	-5 2.6 1.6	-10 -2.0 -2.2
-2 95.7 104.9	8 7.7 8.7	-11 -6.2 -7.0	8 -2.1 -2.1	-4 10.1 8.7	-9 4.3 4.3
0 31.3 28.7	-8 -2.6 -2.3	-10 -5.7 -6.1	11 1 L	-2 -5.5 -4.1	-8 -2.9 -3.1
2 -18.0 -17.5	0 -2.3 -1.1	-9 3.6 3.3	-11 -2.2 -2.9	0 25.9 27.1	-1 3.4 4.8
4 -54.4 -61.7	15 0 L	-8 6.0 4.9	-7 -3.5 -3.7	1 11.5 9.0	0 -2.8 -2.6
6 -7.8 -6.9	8 7.7 8.7	-6 12.4 9.7	-5 2.9 3.4	2 14.1 11.2	1 6.5 5.6
10 -12.8 -15.6	-2 -2.6 -2.3	-5 -19.8 -17.9	-2 -3.3 -2.4	2 2.9 2.6	2 2.9 2.6
12 -6.6 -7.0	0 1 L	-4 -9.8 -7.0	0 -3.4 -1.2	3 -3.9 -4.7	3 -3.9 -4.7
2 0 L	1 38.1 37.2	-3 -10.1 -31.3	2 -8.4 -8.4	4 -3.0 -2.9	4 -3.0 -2.9
-10 -3.2 -5.6	2 16.5 13.3	-2 6.0 4.8	5 3.7 4.2	5 2.0 1.1	5 2.0 1.1
-6 -19.3 -18.3	3 3.7 2.2	-1 -10.4 -8.8	12 1.9 2.3	11 2 L	11 2 L
-4 -56.1 -60.4	4 -11.7 -10.1	0 -6.8 -4.3	4 2 L	-10 -3.0 -5.1	-9 2.7 3.3
2 12.7 12.4	5 -18.5 -16.7	1 -19.3 -15.7	-9 -3.2 -3.7	-5 4.9 4.8	-4 -6.3 -5.7
4 -24.4 -26.5	6 -30.8 -28.2	2 21.1 10.4	-7 -6.6 6.9	-3 3.3 3.7	-1 8.4 7.6
8 -3.4 -1.9	7 -13.4 -11.5	3 -14.0 -12.4	-6 10.9 10.9	1 -13.0 -12.3	2 12.2 11.6
10 -6.4 -8.3	8 -4.9 -4.6	4 -11.1 -11.3	-5 4.9 4.5	3 -5.9 -6.6	3 -5.9 -6.6
3 0 L	9 -3.5 -3.9	7 9.3 9.2	-3 4.3 4.5	-2 -24.4 -22.8	4 2.2 2.8
-12 -11.1 -11.4	12 -4.0 -4.3	8 -20.0 -21.3	0 -1.5 -1.1	1 -27.5 -26.2	12 2 L
-8 -7.3 -7.2	13 -1.9 -1.9	9 13.3 13.6	1 2.7 1.6	2 -8.1 -7.9	-7 4.4 4.5
-4 -50.8 -51.7	14 -2.8 -3.4	10 -6.0 -6.5	2 2.0 2.6	3 31.6 27.0	-5 2.6 2.5
-2 -17.1 -16.7	1 1 L	6 1 L	3 2.3 2.4	4 -30.0 25.1	-3 3.7 3.3
0 58.3 84.8	-13 -2.0 -1.3	-13 -6.1 -6.3	5 -3.1 -3.8	5 -6.1 -4.4	-1 10.0 -9.3
2 -18.6 -20.5	-10 -5.1 -5.2	-11 -5.8 -6.9	13 1 L	6 -6.7 -5.8	0 10.8 10.1
4 6.2 5.8	-9 -6.2 -6.5	-7 12.9 13.6	-8 8.5 10.0	7 2.9 2.3	1 -10.4 -10.1
6 4.3 2.7	-7 -12.7 -10.7	-6 -32.7 -32.3	-7 5.2 5.7	9 -9.3 -8.5	13 2 L
8 12.5 12.9	-6 2.6 2.9	-5 -13.1 -11.9	-6 2.1 2.8	12 -2.6 -2.8	13 2 L
10 8.9 8.5	-5 14.0 12.1	-4 -11.7 -11.1	-5 3.1 3.4	5 2 L	13 2 L
5 0 L	-4 -19.9 -18.0	-3 5.0 3.0	-2 -5.7 -5.5	0 -9.2 -8.3	0 3 L
-4 -9.9 6.9	-2 -21.5 -19.4	-1 7.6 5.8	-1 -7.6 -5.8	1 41.9 37.4	1 8.4 7.8
-2 18.5 18.3	-1 36.4 36.0	0 23.7 21.2	1 -3.6 -3.6	2 15.5 12.2	2 3.2 3.3
0 -4.0 -2.6	-2 -10.0 -10.0	1 18.4 16.5	14 1 L	3 3.2 3.2	3 17.8 15.0
2 -6.9 -6.9	-4 13.1 11.0	2 -12.2 -12.4	-4 1.7 1.8	4 -2.6 -2.4	4 3.5 2.7
4 12.1 13.1	-2 20.2 22.6	3 7.5 6.8	-4 -3.4 -4.5	5 6.1 4.9	6 -12.4 -11.4
6 4.2 0.8	0 2.8 3.1	5 -7.2 -6.3	-2 -9.4 -7.4	6 5.6 5.6	7 31.3 31.3
8 14.5 14.8	2 7.5 7.3	6 -4.7 4.8	-1 -3.1 -3.4	7 -12.4 -11.4	7 31.3 31.3
6 0 L	6 12.5 12.9	7 10.1 10.6	-1 -18.0 -17.4	8 -5.8 -4.8	8 5.8 5.2
-12 -2.3 -2.0	10 8.9 8.5	7 1 L	0 -7.2 -6.7	9 -2.7 3.5	9 -2.7 3.5
-8 16.5 16.2	5 0 L	-13 -3.4 -3.8	1 41.9 37.4	11 2.7 3.5	11 -3.8 -4.8
-4 14.8 14.5	-4 -5.9 6.9	-9 13.6 14.6	2 15.5 12.2	6 2 L	11 -3.8 -4.8
-2 -9.1 -7.9	-2 18.5 18.3	-8 -9.8 -9.3	3 -3.2 -3.1	7 12.4 11.4	12 5.1 4.1
0 -25.3 -23.7	0 -4.0 -2.6	-7 11.5 11.3	4 -2.6 -2.4	8 5.6 5.6	13 -8.0 -8.9
6 -3.1 -4.1	2 -6.9 -6.6	-6 -9.8 -9.3	5 18.0 15.1	9 -5.8 -4.8	1 3 L
8 -6.8 -8.2	4 12.1 13.1	-4 4.5 3.3	6 9.0 6.4	11 2.7 3.5	1 3 L
8 0 L	6 4.2 0.8	-3 -15.1 -12.2	7 11.6 9.9	6 2 L	1 3 L
-12 -2.3 -2.0	8 14.5 14.8	-2 -23.6 -20.8	8 5.3 4.5	-13 5.6 5.4	1 3 L
-8 16.5 16.2	6 0 L	-1 27.3 -29.8	9 5.0 4.3	-12 -8.1 -8.1	1 3 L
-4 14.8 14.5	2 59.9 65.4	0 5.2 3.1	3 -12.1 -11.8	-11 3.7 -3.9	1 3 L
-2 -9.1 -7.9	3 16.6 16.2	4 12.7 12.2	4 12.7 12.2	10 -3.7 -3.8	-13 -6.4 -6.8
0 -25.3 -23.7	4 -11.3 -9.4	5 -6.9 -6.6	6 4.7 4.7	-9 4.7 4.4	-10 -5.6 -4.9
6 -3.1 -4.1	5 11.4 10.9	-8 -9.8 -9.3	13 1 L	-7 -5.5 -4.1	-9 32.6 33.7
8 -6.8 -8.2	6 4.3 2.7	-4 -4.5 3.2	0 3.3 2.9	-6 -6.4 -5.6	-8 6.2 5.6
8 0 L	8 -5.2 -2.2	-3 -15.1 -12.2	7 1 L	-7 -5.4 -4.0	-7 32.3 32.9
-12 -2.3 -2.0	10 4.4 4.3	-2 -21.7 -18.9	8 12.9 12.2	-1 17.7 14.7	-6 8.1 7.6
-8 16.5 16.2	13 -5.0 -4.6	-1 8.7 8.0	9 6.9 6.9	0 -40.0 39.1	7 -4.6 4.8
-4 14.8 14.5	10 16.7 20.7	1 5.0 4.3	10 4.0 3.2	11 2.7 3.5	-4 6.3 4.9
-2 -9.1 -7.9	0 -16.7 -15.8	2 2.3 1.4	12 -7.2 -5.4	6 2 L	-3 -25.2 -20.3
0 -25.3 -23.7	4 -19.0 -19.6	3 -12.1 -11.8	13 4.1 3.6	7 12.4 11.4	-2 -11.1 -8.6
6 -3.1 -4.1	6 -5.2 -5.9	4 12.7 12.2	0 2 L	8 -5.8 -4.8	0 -1.2 -0.1
8 -6.8 -8.2	8 14.5 14.8	5 -6.9 -6.6	1 41.9 37.4	9 -2.7 3.5	0 -2.4 -1.7
8 0 L	10 16.7 20.7	6 4.7 4.7	2 15.5 12.2	11 2.7 3.5	1 13.1 12.1
-12 -2.3 -2.0	0 -16.7 -15.8	7 11.5 11.3	3 -3.2 -3.1	6 2 L	2 11.2 9.6
-8 16.5 16.2	4 -19.0 -19.6	-4 4.5 3.3	4 -3.6 -2.7	7 12.4 11.4	3 -41.4 -39.9
-4 14.8 14.5	6 -5.2 -5.9	-3 -15.1 -12.2	5 18.0 15.1	8 5.6 5.6	4 -6.2 -4.9
-2 -9.1 -7.9	8 14.5 14.8	-2 -21.7 -18.9	6 9.0 6.4	9 -5.8 -4.8	5 -13.8 -12.4
0 -25.3 -23.7	10 16.7 20.7	-1 8.7 8.0	7 11.6 9.9	11 2.7 3.5	6 -1.5 -1.5
6 -3.1 -4.1	0 -16.7 -15.8	1 5.0 4.3	8 5.3 4.5	6 2 L	6 -1.5 -1.5
8 -6.8 -8.2	4 -19.0 -19.6	2 2.3 1.4	9 5.0 4.3	-13 5.6 5.4	7 -4.6 4.8
8 0 L	6 -5.2 -5.9	3 -12.1 -11.8	10 4.0 3.2	-12 -8.1 -8.1	8 5.8 5.2
-12 -2.3 -2.0	8 14.5 14.8	4 12.7 12.2	12 -7.2 -5.4	-11 3.7 -3.9	9 10.6 10.6
-8 16.5 16.2	10 16.7 20.7	5 -6.9 -6.6	13 4.1 3.6	10 -3.7 -3.8	10 6.7 7.2
-4 14.8 14.5	0 -16.7 -15.8	6 4.7 4.7	0 2 L	11 2.7 3.5	11 -3.3 -3.9
-2 -9.1 -7.9	4 -19.0 -19.6	7 11.5 11.3	1 41.9 37.4	6 2 L	11 -3.3 -3.9
0 -25.3 -23.7	6 -5.2 -5.9	-4 4.5 3.3	2 15.5 12.2	7 12.4 11.4	12 5.1 4.1
6 -3.1 -4.1	8 14.5 14.8	-3 -15.1 -12.2	3 -3.2 -3.1	8 5.6 5.6	13 -8.0 -8.9
8 -6.8 -8.2	10 16.7 20.7	-2 -21.7 -18.9	4 -2.6 -2.4	9 -5.8 -4.8	1 3 L
8 0 L	0 -16.7 -15.8	-1 8.7 8.0	5 18.0 15.1	11 2.7 3.5	1 3 L
-12 -2.3 -2.0	4 -19.0 -19.6	1 5.0 4.3	6 9.0 6.4	6 2 L	1 3 L
-8 16.5 16.2	6 -5.2 -5.9	2 2.3 1.4	7 11.6 9.9	-13 5.6 5.4	1 3 L
-4 14.8 14.5	8 14.5 14.8	3 -12.1 -11.8	8 5.3 4.5	-12 -8.1 -8.1	1 3 L
-2 -9.1 -7.9	10 16.7 20.7	4 12.7 12.2	9 5.0 4.3	-11 3.7 -3.9	1 3 L
0 -25.3 -23.7	0 -16.7 -15.8	5 -6.9 -6.6	10 4.0 3.2	10 -3.7 -3.8	1 3 L
6 -3.1 -4.1	4 -19.0 -19.6	6 4.7 4.7	12 -7.2 -5.4	11 2.7 3.5	1 3 L
8 -6.8 -8.2	6 -5.2 -5.9	7 11.5 11.3	13 4.1 3.6	6 2 L	1 3 L
8 0 L	8 14.5 14.8	-4 4.5 3.3	0 2 L	7 12.4 11.4	1 3 L
-12 -2.3 -2.0	10 16.7 20.7	-3 -15.1 -12.2	1 41.9 37.4	8 5.6 5.6	1 3 L
-8 16.5 16.2	0 -16.7 -15.8	-2 -21.7 -18.9	2 15.5 12.2	9 -5.8 -4.8	1 3 L
-4 14.8 14.5	4 -19.0 -19.6	-1 8.7 8.0	3 -3.2 -3.1	11 2.7 3.5	1 3 L
-2 -9.1 -7.9	6 -5.2 -5.9	1 5.0 4.3	4 -3.6 -2.7	6 2 L	1 3 L
0 -25.3 -23.7	8 14.5 14.8	2 2.3 1.4	5 18.0 15.1	7 12.4 11.4	1 3 L
6 -3.1 -4.1	10 16.7 20.7	3 -12.1 -11.8	6 9.0 6.4	8 5.6 5.6	1 3 L
8 -6.8 -8.2	0 -16.7 -15.8	4 12.7 12.2	7 11.6 9.9	9 -5.8 -4.8	1 3 L
8 0 L	4 -19.0 -19.6	5 -6.9 -6.6	8 5.3 4.5	11 2.7 3.5	1 3 L
-12 -2.3 -2.0	6 -5.2 -5.9	6 4.7 4.7	9 5.0 4.3	6 2 L	1 3 L
-8 16.5 16.2	8 14.5 14.8	7 11.5 11.3	10 4.0 3.2	-13 5.6 5.4	1 3 L
-4 14.8 14.5	10 16.7 20.7	-4 4.5 3.3	12 -7.2 -5.4	-12 -8.1 -8.1	1 3 L
-2 -9.1 -7.9	0 -16.7 -15.8	-3 -15.1 -12.2	13 4.1 3.6	-11 3.7 -3.9	1 3 L
0 -25.3 -23.7	4 -19.0 -19.6	-2 -21.7 -18.9	0 2 L	10 -3.7 -3.8	1 3 L
6 -3.1 -4.1	6 -5.2 -5.9	-1 8.7 8.0	1 41.9 37.4	11 2.7 3.5	1 3 L
8 -6.8 -8.2	8 14.5 14.8	1 5.0 4.3	2 15.5 12.2	6 2 L	1 3 L
8 0 L	10 16.7 20.7	2 2.3 1.4	3 -3.2 -3.1	7 12.4 11.4	1 3 L
-12 -2.3 -2.0	0 -16.7 -15.8	3 -12.1 -11.8	4 -3.6 -2.7	8 5.6 5.6	1 3 L
-8 16.5 16.2	4 -19.0 -19.6	4 12.7 12.2	5 18.0 15.1	9 -5.8 -4.8	1 3 L
-4 14.8 14.5	6 -5.2 -5.9	5 -6.9 -6.6	6 9.0 6.4	11 2.7 3.5	1 3 L
-2 -9.1 -7.9	8 14.5 14.8	6 4.7 4.7	7 11.6 9.9	6 2 L	1 3 L
0 -25.3 -23.7	10 16.7 20.7	7 11.5 11.3	8 5.3 4.5	-13 5.6 5.4	1 3 L
6 -3.1 -4.1	0 -16.7 -15.8	-4 4.5 3.3	9 5.0 4.3	-12 -8.1 -8.1	1 3 L
8 -6.8 -8.2	4 -19.0 -19.6	-3 -15.1 -12.2	10 4.0 3.2	-11 3.7 -3.9	1 3 L
8 0 L	6 -5.2 -5.9	-2 -21.7 -18.9	12 -7.2 -5.4	10 -3.7 -3.8	1 3 L
-12 -2.3 -2.0	8 14.5 14.8	-1 8.7 8.0	13 4.1 3.6	11 2.7 3.5	1 3 L
-8 16.5 16.2	10 16.7 20.7	1 5.0 4.3	0 2 L	6 2 L	1 3 L
-4 14.8 14.5	0 -16.7 -15.8	2 2.3 1.4	1 41.9 37.4	7 12.4 11.4	1 3 L
-2 -9.1 -7.9	4 -19.0 -19.6	3 -12.1 -11.8	2 15.5 12.2	8 5.6 5.6	1 3 L
0 -25.3 -23.7	6 -5.2 -5.9	4 12.7 12.2	3 -3.2 -3.1	9 -5.8 -4.8	1 3 L
6 -3.1 -4.1	8 14.5 14.8	5 -6.9 -6.6	4 -3.6 -2.7	11 2.7 3.5	1 3 L
8 -6.8 -8.2	10 16.7 20.7	6 4.7 4			



bonyl group. In quinhydrone, the hydrogen bond forms an infinite molecular chain along the [120] direction, while in phenoquinone one quinone molecule is placed between two phenol molecules to form a short complex chain as shown in Fig. 2. These chains are packed side by side to form a molecular sheet. All molecular planes in the sheet are almost parallel. The distance between the molecular planes in a sheet is about 3.2 Å, which exhibits a typical charge transfer interaction

between the chain. The best-fit planes through these molecules are

$$0.8435x - 0.4987y - 0.4757z = 3.225$$

and

$$0.8090x - 0.5436y - 0.4864z = 0$$

for quinone and hydroquinone respectively in quinhydrone, and

$$0.8312x + 0.4849y + 0.1235z = 0$$

Table 3. Atomic parameters for quinhydrone

Expression of the temperature factor: $\exp [-(B_{11}h^2 + B_{22}k^2 + B_{33}l^2 + 2B_{12}hk + 2B_{23}kl + 2B_{31}lh)]$									
	$x/a$	$y/b$	$z/c$	$B_{11}$	$B_{22}$	$B_{33}$	$B_{12}$	$B_{23}$	$B_{31}$
	$\times 10^{-2}$								
Hydroquinone									
O(1)	0.2588	0.3336	0.0901	1.33	1.32	0.46	-0.68	0.12	-0.14
C(1)	0.1274	0.1706	0.0429	0.75	0.98	0.39	-0.20	0.17	-0.07
C(2)	0.1140	0.0056	0.1220	0.81	1.57	0.31	-0.06	0.11	0.06
C(3)	0.0151	0.1664	-0.0797	0.95	1.32	0.37	-0.09	0.16	0.19
H(1)	0.269	0.410	0.048						
H(2)	0.214	0.016	0.214						
H(3)	0.046	0.289	-0.134						
Quinone									
O(2)	0.7233	0.3478	0.0746	1.48	1.23	0.48	-0.68	0.22	-0.20
C(4)	0.6216	0.1869	0.0395	0.84	1.12	0.36	-0.12	0.18	-0.06
C(5)	0.6148	0.0096	0.1260	0.97	1.41	0.30	-0.14	0.13	0.02
C(6)	0.5010	0.1629	-0.0903	0.94	1.48	0.35	-0.14	0.14	0.14
H(4)	0.715	0.030	0.209						
H(5)	0.540	0.283	-0.144						
Standard deviations									
O	0.0005	0.0007	0.0004	0.08	0.12	0.03	0.08	0.04	0.05
C	0.0007	0.0010	0.0005	0.09	0.15	0.04	0.10	0.05	0.07
H	0.010	0.015	0.007						

Table 4. Atomic parameters for phenoquinone

Expression of the temperature factor: $\exp [-(B_{11}h^2 + B_{22}k^2 + B_{33}l^2 + 2B_{12}hk + 2B_{23}kl + 2B_{31}lh)]$									
	$x/a$	$y/b$	$z/c$	$B_{11}$	$B_{22}$	$B_{33}$	$B_{12}$	$B_{23}$	$B_{31}$
	$\times 10^{-2}$								
Quinone									
O(1)	0.0906	-0.3540	0.1253	0.73	1.13	0.60	0.24	0.09	0.37
C(1)	0.0492	-0.1897	0.0674	0.47	1.08	0.48	0.04	0.04	0.12
C(2)	0.0138	0.0111	-0.1205	0.65	1.31	0.45	0.11	0.12	-0.05
C(3)	0.0619	-0.1660	-0.0580	0.53	1.31	0.45	0.08	0.07	-0.03
H(1)	0.017	0.027	-0.220						
H(2)	0.109	-0.289	-0.095						
Phenol									
O(2)	0.2238	0.3285	0.0259	0.97	1.22	0.70	0.21	0.16	0.34
C(4)	0.2790	0.1607	0.0975	0.45	1.15	0.56	-0.09	0.06	-0.01
C(5)	0.2728	0.1495	0.2167	0.58	1.64	0.63	0.04	0.08	-0.15
C(6)	0.3278	-0.0291	0.2835	0.56	2.29	0.61	0.00	0.03	0.10
C(7)	0.3888	-0.1935	0.2308	0.63	1.94	0.85	0.18	-0.06	0.30
C(8)	0.3959	-0.1805	0.1138	0.66	1.98	0.84	0.39	-0.01	0.22
C(9)	0.3406	-0.0018	0.0456	0.57	1.97	0.60	0.04	0.07	-0.15
H(3)	0.184	0.389	0.064						
H(4)	0.221	0.243	0.264						
H(5)	0.334	-0.049	0.384						
H(6)	0.436	-0.313	0.282						
H(7)	0.455	-0.291	0.067						
H(8)	0.341	0.029	-0.054						
Standard deviations									
O	0.0004	0.0007	0.0004	0.05	0.11	0.04	0.06	0.04	0.06
C	0.0006	0.0011	0.0006	0.06	0.18	0.06	0.08	0.05	0.08
H	0.007	0.013	0.006						

and

$$0.8178x + 0.5340y + 0.0697z = 3.126$$

for quinone and phenol respectively in phenoquinone.

None of the carbon-carbon distances between different molecular sheets is shorter than 3.7 Å. Short carbon-oxygen distances, being around 3.3 Å, are shown in Fig. 1(a) and (b). These are within the range of the ordinary van der Waals distance.

#### Molecular structure

Bond distances and angles are shown in Fig. 3. These values are corrected for the effect of rigid body vibrations (Busing & Levy, 1964); the magnitudes of these corrections are shown in parentheses. A remarkable deformation of the benzenoid ring of the hydroquinone was reported by Matsuda *et al.* Such a deformation, however, is not observed in the present case. In  $\beta$ -quinhydrone a significant difference between the C-C-OH bond angles on the hydrogen side and those on the non-hydrogen side was observed. A similar difference is also found in the present compounds. Therefore, it can be concluded that the C-C-OH bond angles depend on the direction of the O-H bond. The mean C-C-OH structure averaged over  $\alpha$ -quinhydrone,  $\beta$ -quinhydrone and phenoquinone is shown in Fig. 4. This result is consistent with those obtained for  $\gamma$ -hydroquinone and phloroglucinol (Maartmann-Moe, 1966, 1965).

#### Distances related to the charge transfer interaction

Intermolecular atomic distances in a molecular sheet are shown in Fig. 5. Angles between the molecular planes and several important distances are shown in Table 5.

It is well known that the stability of the complexes formed by the same acceptor increases with decreasing ionization potentials of donors (Mulliken, 1952). The ionization potential of phenol is 8.50 eV (Watanabe, 1957), and that of hydroquinone is estimated to be 7.70 eV (Kunii, 1967). In spite of this difference of ionization potential, no essential difference exists in the perpendicular separation or the inter-planar atomic distances. However, a significant difference is found in the distance connecting the carbon ring centers (last column of Table 5). This agrees with the result of Annex (1963), who showed from reflection spectroscopy of  $\alpha$ -quinhydrone that the transition moment is not perpendicular to the carbon ring but rather lies along a line joining the ring centers.

#### Charge integration

The total charge of the molecule for  $\alpha$ -quinhydrone can be obtained by a similar procedure to that used for  $\beta$ -quinhydrone (Sakurai, 1965). For the purpose of the charge integration, the crystal axes are transformed

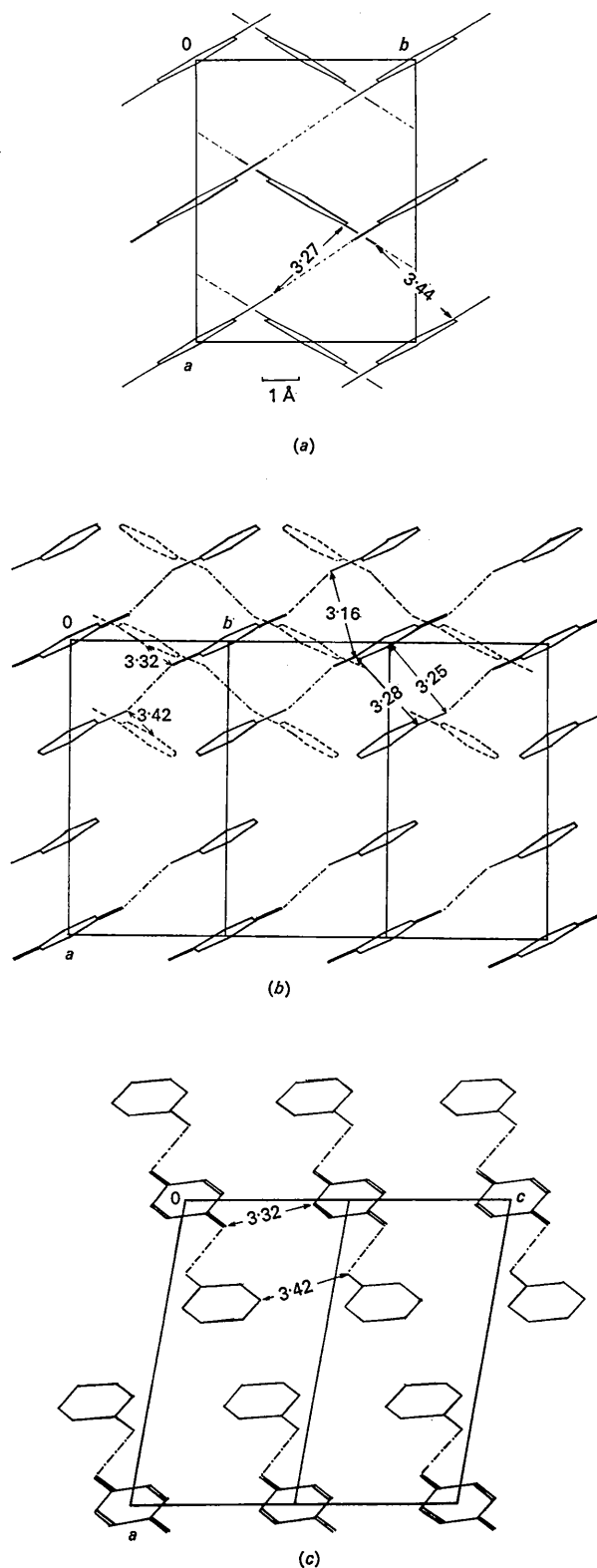


Fig. 1. Crystal structures. (a) Quinhydrone. Projection along the [101] axis. (b) Phenoquinone. Projection along the *c* axis. (c) Phenoquinone. Projection along the *b* axis.

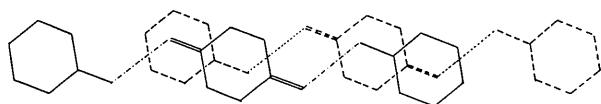


Fig. 2. Arrangement of the molecular chain in phenoquinone, viewed from the normal to the molecular plane.

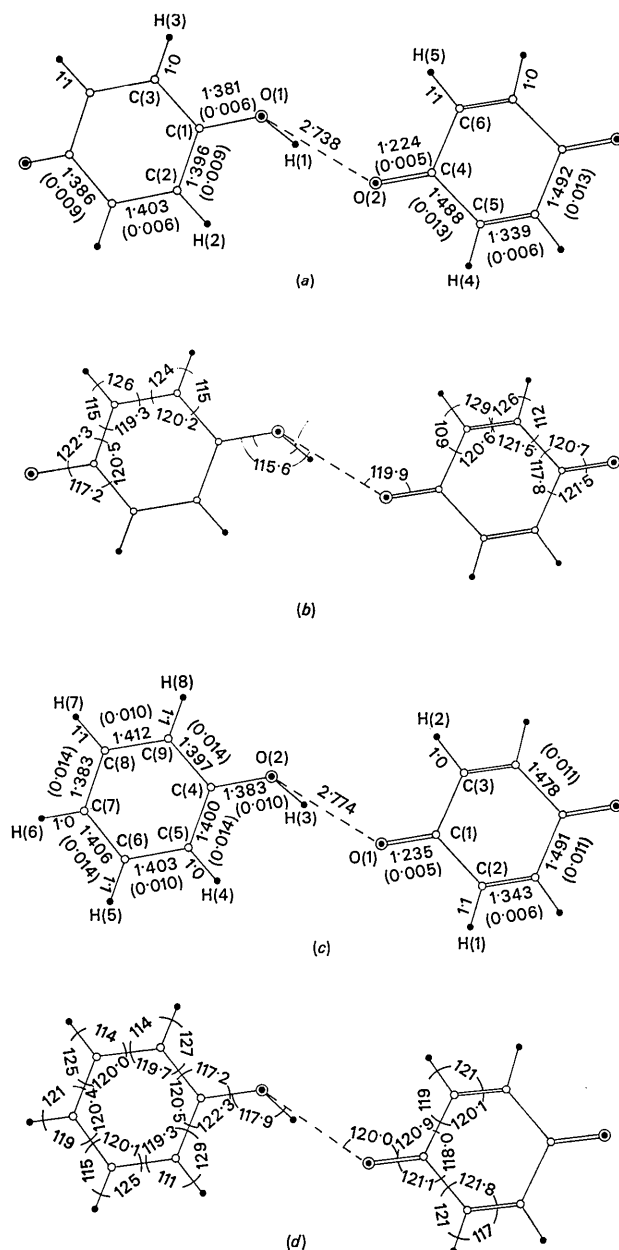


Fig. 3. Bond distances and angles. Encircled dots: oxygen; small open circles: carbon; black dots: hydrogen. (a) Bond distances in quinhydrone.  $\sigma(\text{C}-\text{O})=0.007$ ,  $\sigma(\text{C}-\text{C})=0.008$ ,  $\sigma(\text{C}-\text{H})=0.09$  Å. (b) Bond angles in quinhydrone.  $\sigma(\text{O}-\text{C}-\text{C})=0.5$ ,  $\sigma(\text{C}-\text{C}-\text{C})=0.5$ ,  $\sigma(\text{C}-\text{C}-\text{H})=4^\circ$ . (c) Bond distances in phenoquinone.  $\sigma(\text{C}-\text{O})=0.007$ ,  $\sigma(\text{C}-\text{C})=0.010$ ,  $\sigma(\text{C}-\text{H})=0.08$  Å. (d) Bond angles in phenoquinone.  $\sigma(\text{O}-\text{C}-\text{C})=0.6$ ,  $\sigma(\text{C}-\text{C}-\text{C})=0.6$ ,  $\sigma(\text{C}-\text{C}-\text{H})=4^\circ$ .

into a new system  $a', b', c'$ , where the transformation of the axes and the index is expressed by

$$\begin{aligned} a' &= a - b & h' &= h - k \\ b' &= a + 2b & k' &= h + 2k \\ c' &= a + c & l' &= h + l \end{aligned}$$

Then the total charges of the hydroquinone and quinone molecules are given by (Fig. 6)

$$Q_h = \int_{-(1/4)c'}^{(1/4)c'} \int_{-(1/4)b'}^{(1/4)b'} \int_{-(1/6)a'}^{(1/6)a'} \rho dv = \frac{1}{12} F_{0'0'0'} + \sum' A_1 A_2 A_3 F_{h'k'l'}$$

$$\text{and } Q_q = \int_{-(1/4)c'}^{(1/4)c'} \int_{(1/4)b'}^{(3/4)b'} \int_{-(1/6)a'}^{(1/6)a'} \rho dv = \frac{1}{12} F_{0'0'0'} - \sum' A_1 A_2 A_3 F_{h'k'l'}$$

respectively, where  $A_1$ ,  $A_2$  and  $A_3$  are given in Table 6.

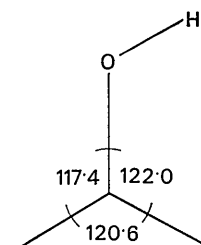


Fig. 4. Mean C-C-OH structure.

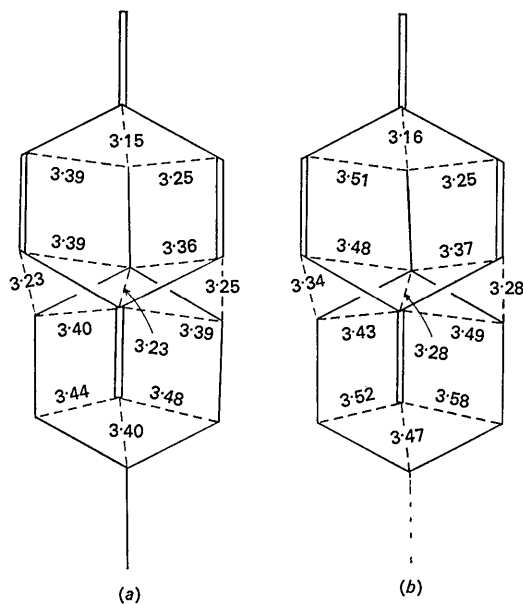


Fig. 5. Interatomic distances between molecular planes. (a) Quinhydrone. (b) Phenoquinone.

Table 5. Angles and distances between molecular planes

Crystal	Angle between molecular planes	Perpendicular distance	Shortest atomic distance		Distance between the carbon ring centers
			C-C	C-O	
$\alpha$ -Quinhydrone	3.5°	3.22 Å	3.17 Å	3.25 Å	3.82 Å
$\beta$ -Quinhydrone	2.0	3.19	3.18	3.26	3.83
Phenoquinone	4.5	3.13	3.16	3.25	3.99

Table 6. Coefficients of charge integration

$h'$	$A_1$	$k'$	$A_2$	$l'$	$A_3$
0	$\frac{1}{2}a'$	0	$\frac{1}{2}b'$	0	$\frac{1}{2}c'$
$6n+1$ $6n+2$ }	$\frac{3}{2\pi h'} a' 4n+1$		$\frac{1}{\pi k'} b' 4n+1$	$4n+1$	$\frac{1}{\pi l'} c' 4n+1$
$6n+3$	0	$4n+2$	0	$4n+2$	0
$6n+4$ $6n+5$ }	$-\frac{3}{2\pi h'} a' 4n+3$		$-\frac{1}{\pi k'} b' 4n+3$	$4n+3$	$-\frac{1}{\pi l'} c' 4n+3$
$6n$	0	$4n$	0	$4n$	0

It should be noted that the above transformation changes the original monoclinic cell into a triclinic big cell. Therefore, the summation must be carried out through the whole reciprocal space of the big cell. It is easily seen from the condition in Table 6 that the reflections with  $h$  even (strong reflections) do not contribute to the charge integral. The result of the integration is

$$Q_n = \frac{1}{12} F_{0'0'0'} + 0.29, \quad Q_a = \frac{1}{12} F_{0'0'0'} - 0.29.$$

Therefore, the amount of transferred charge from hydroquinone to quinone is 0.71 electron. This value is considerably larger than the value 0.21 found in  $\beta$ -quinhydrone. Because one of the hydrogen atoms is near the boundary of integration (Fig. 6), it is probable that the range of the above integrals does not correspond to the true boundary of the molecule. Further, if the boundary is shifted from  $\frac{1}{4}c'$ , all strong reflections with  $h$  even should also be considered. In view of these circumstances, it is known that this structure corresponds to the case in which the estimation of the transferred charge is more difficult than for  $\beta$ -quinhydrone.

Thus, in order to obtain a more reliable value a considerably more accurate measurement is necessary.

#### Thermal vibrations

Ellipsoids of thermal vibration are shown in Fig. 7. These are transformed into a rigid body vibration of the molecule. The results are shown in Table 7. Axes of the molecular vibration are shown in Fig. 8. General agreement between observed and calculated mean square displacements is good, except for the  $U_{11}$  component of the oxygen atoms. This point will be discussed elsewhere.

#### Computation

The main part of the numerical calculations was performed on the HITAC 5020 computer of the computer center of the University of Tokyo, using universal crystallographic computation program system 5020 UNICS (Sakurai, Ito, Iwasaki & Watanabe, 1967). Fig. 7(a) and 7(b) are drawn with a plotter from the direct output of the IBM 7090 computer using ORTEP (Johnson, 1965).

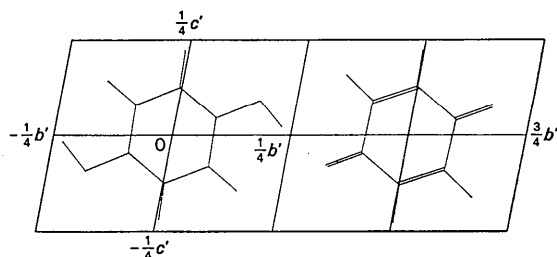


Fig. 6. Boundary of charge integration for quinhydrone.

Table 7. Tensors of rigid body vibration of molecules

Molecule	Translational	Rotational
Hydroquinone in quinhydrone	$\begin{pmatrix} 1.7 & 0 & 0.2 \\ 0 & 1.8 & 0.1 \\ 0.2 & 0.1 & 1.5 \end{pmatrix} 10^{-2} \text{Å}^2$	$\begin{pmatrix} 29 & -3 & 9 \\ -3 & 14 & 1 \\ 9 & 1 & 6 \end{pmatrix} \text{deg.}$
Quinone in quinhydrone	$\begin{pmatrix} 1.8 & 0 & 0.2 \\ 0 & 1.8 & 0 \\ 0.2 & 0 & 1.4 \end{pmatrix}$	$\begin{pmatrix} 32 & -2 & 8 \\ -2 & 15 & 2 \\ 8 & 2 & 7 \end{pmatrix}$
Phenol in phenoquinone	$\begin{pmatrix} 2.8 & -0.6 & 0.4 \\ -0.6 & 3.6 & 0.3 \\ 0.4 & 0.3 & 1.8 \end{pmatrix}$	$\begin{pmatrix} 36 & -7 & 14 \\ -7 & 23 & 0 \\ 14 & 0 & 16 \end{pmatrix}$
Quinone in phenoquinone	$\begin{pmatrix} 1.9 & -0.2 & 0.4 \\ -0.2 & 2.6 & 0.3 \\ 0.4 & 0.3 & 1.8 \end{pmatrix}$	$\begin{pmatrix} 28 & 7 & 1 \\ 7 & 12 & 1 \\ 1 & 1 & 9 \end{pmatrix}$



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pursue these refinements. A part of this work is supported by financial aid from the Ministry of Education.

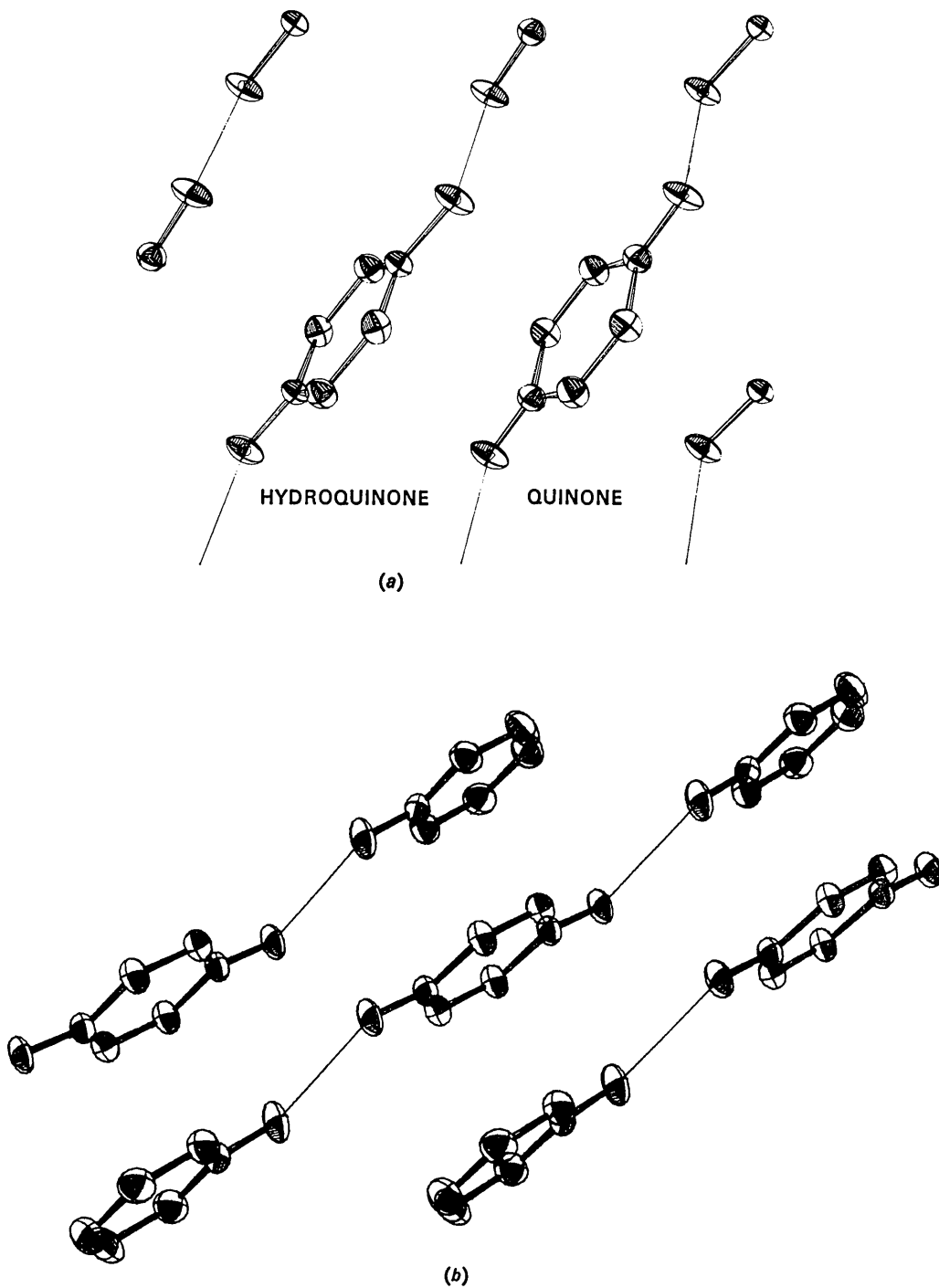


Fig. 7. Ellipsoids of thermal vibration. (a) Quinhydrone. (b) Phenoquinone.

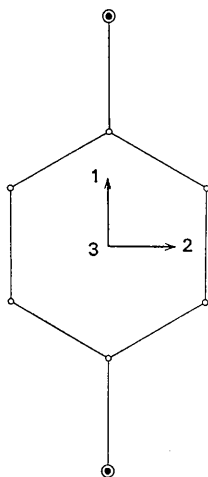


Fig. 8. Axes of the rigid body vibration.

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### The Crystal Structure of Nb<sub>21</sub>S<sub>8</sub>\*

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The crystal structure of Nb<sub>21</sub>S<sub>8</sub> has been determined from single-crystal X-ray diffraction data. The compound crystallizes in the tetragonal system, space group *I4/m* with unit-cell parameters  $a = 16.794 \text{ \AA}$ ,  $c = 3.359 \text{ \AA}$ . The unit cell contains two formula units. All atoms are located in layers separated by  $c/2$ . Refinement of the structure was performed by least-squares treatment of  $x$  and  $y$  positional parameters and isotropic temperature factor coefficients. Pauling bond orders indicate that the coordination of sulfur in this compound is seven. This result is consistent with sulfur atoms utilizing  $d$  orbitals to form electron deficient bonds to the metal atoms.

#### Introduction

The high temperature (*ca.* 1350°C) preparation of a new subsulfide in the niobium-sulfur system, characterized as Nb<sub>2</sub>S, and some crystallographic data for the compound were recently reported (Franzen, DeJong & Conard, 1966). The compositions reported were obtained by combustion techniques on samples which have since been identified as containing two phases. A more recent composition analysis is reported below.

Previous studies of the niobium-sulfur system in the range  $0 \leq S/Nb \leq 1.0$  resulted in the identification of two phases, neither of which was the same as the phase reported here. Biltz & Köcher (1938) reported a phase with the homogeneity range  $0.5 \leq S/Nb \leq 1.0$ ; Jellinek

(1962) observed a NbS<sub>1-x</sub> ( $x = 0.1$  to ?) phase with an ordered NiAs-type structure.

Investigations of the lower sulfides of Hf and Ti, namely Hf<sub>2</sub>S (Franzen & Graham, 1966) and Ti<sub>2</sub>S (Owens, Conard & Franzen, 1966), have resulted in a new interpretation of the bonding of sulfur in the mono-sulfides and lower sulfides of transition metals (Franzen, 1966). The interest in the crystal structure of Nb<sub>21</sub>S<sub>8</sub> stemmed from a desire to describe more completely the chemistry of sulfur in the lower sulfides of transition metals.

#### Experimental

The previously reported crystallographic data for Nb<sub>21</sub>S<sub>8</sub> are summarized as follows. The space group was reported to be *I4/m*, the lattice parameters reported were  $a = 16.794 \pm 0.005$ ,  $c = 3.359 \pm 0.002 \text{ \AA}$ , and the number of 'Nb<sub>2</sub>S' formula units per unit cell was estimated to be between 21 and 24, based on a measured

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