Crystal Structure of Quinhydrone, $C_{12}H_{10}O_4$

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The peculiar properties of some aromatic molecular compounds and the question as to the forces responsible for their formation have been attracting the attention of a number of authors. Anderson(1) investigated a series of molecular compounds containing quinone, or its derivatives, and concluded that in all these compounds the component molecules are alternately stacked plane to plane, and that the most probable mechanism for the binding is effected by the interaction between strongly polar groups and by the highly anisotropic and polarizable aromatic systems. Such a type of parallel stacking was also found in *p*-iodoaniline-*s*-trinitrobenzene(2) which was the first example fully analyzed among the aromatic molecular compounds. For the discussion of the nature of intermolecular attraction, however, it is very desirable to obtain more data on inter- and intra-molecular distances and bond angles in these aromatic molecular compounds.**

Quinhydrone, or benzoquinhydrone, is the simplest of the series of molecular compounds containing quinones. It is highly desirable to determine its structure in detail, though there have been published a few papers which describe the general arrangement of molecules in this crystal.

Palacios and Foz reported in their first paper(3) that the monoclinic unit cell ($\beta = 90°$) of quinhydrone contains one formula unit $C_{12}H_{10}O_4$ and the molecules are linked in endless chains by symmetrical hydrogen bonding. This structure in which both the molecules of quinone and hydroquinone are placed in the same equivalent positions, so that they are not distinguishable, was however revised by the same authors(4).

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* Deceased 1950. This work, especially the most laborious part of it, was almost completed by H. Matsuda. It was continued and written up after his death.

1) J. S. Anderson, *Nature*, **140**, 583 (1937).

2) H. M. Powell, G. Huse and P. W. Cooke, *J. Chem. Soc.*, **1943**, 153.

** When the present work was almost completed, Dr. Wallwork was so kind as to inform us of his detailed analysis of phenoquinone. See S. C. Wallwork and T. T. Harding, *Nature*, **171**, 40; T. T. Harding and S. C. Wallwork, *Acta Cryst.*, **6**, 791 (1953); **8**, 787 (1955).

3) O. R. Foz and J. Palacios, *Anales Soc. Españ. Fis. Quim.*, **30**, 421 (1932).

4) J. Palacios and O. R. Foz., *Anales Soc. Españ. Fis. Quim.*, **33**, 627 (1935); **34**, 779 (1936).

They observed weak superstructure reflections requiring doubled a and c axes, and they ascribed the observed subperiodicity to the discrete existence of quinoid and quinoloid units in the structure. This view is in accord with that of Anderson quoted above.[1]

Preliminary Investigations.—Most of the well-defined, apparently single crystals grown from acetone solutions have the appearance of hexagonal prisms. Laue photographs showed, however, that they are twins, and that the axial angle β was not exactly equal to 90° as has been reported. The deviation was estimated from the separation of Laue spots to be about 45′. Single crystals were easily obtained by splitting these twins with the aid of a razor blade and were used for subsequent works.

Lattice constants, derived from a series of symmetrical back reflection photographs, are

$$a=7.674\pm0.001\text{Å},\quad b=6.001\pm0.001\text{Å}$$
$$c=21.788\pm0.002\text{Å},\quad \beta=90°38'\pm3'.$$

Four $C_{12}H_{10}O_4$ units are contained in this lattice and the calculated density is 1.444 g./cm^3 as compared with the observed value 1.401 at 20°C. Systematic extinctions were observed in (hkl) when $h+l$ is odd, in $(0k0)$ when k is odd and in $(h0l)$ when $h-l$ is not multiple of 4. The only space group which conforms to these rules is $C_{2h}^5-B2_1/d$ with the glide translation $(a-c)/4$ for the above set of axes. The symmetry elements of this space group are shown in Fig. 1, and general and special point positions are listed in Table I. This lattice can be reduced to another having $a=7.647$ Å, $b=6.001$ Å, $c'=11.590$ Å and $\beta'=109°58'$ expressed in terms of $P2_1/c$, if we take the c'-axis as indicated in Fig. 1. Although this expression is more common, the former one ($\beta\approx90°$) was adopted throughout this work for the sake of convenience.

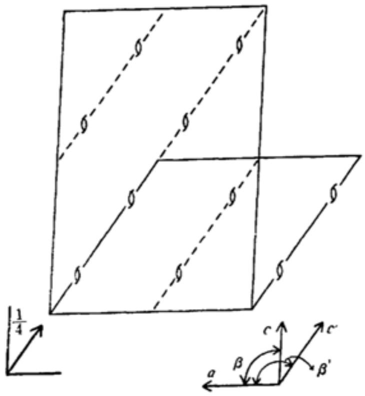

Fig. 1. Unit cell and symmetry elements of $B2_1/d$ and its reduction to $P2_1/c$.

Determination of the Averaged Structure.—A characteristic feature of the X-ray pattern of quinhydrone, as has been reported by Palacios and Foz, is that all the reflections with h, l odd are very weak, compared with those with h, l even. If we construct a Fourier representation of such a structure using even reflections alone, we shall obtain a hypothetical averaged structure repeating with lattice dimensions $(1/2)\,a$, b and $(1/2)\,c$. This averaged structure will be a fairly good approximation to the "true" structure, since reflections with h, l odd are all weak and will not contribute much to the Fourier representation of the true structure. Therefore first we determined this averaged structure and then proceeded to the true one.

The hypothetical averaged structure introduced above contains only one sort

TABLE I

GENERAL AND SPECIAL POINT POSITIONS FOR THE ADOPTED SPACE GROUP $B2_1/d$

8-fold general positions

$$8\ (\mathrm{e}):\ \pm\left[\begin{array}{lcl} x,\ y,\ z & ; & \frac{1}{2}+x,\ y,\ \frac{1}{2}+z\ ; \\ \frac{1}{4}+x,\ \frac{1}{2}-y,\ \frac{3}{4}+z & ; & \frac{3}{4}+x,\ \frac{1}{2}-y,\ \frac{1}{4}+z. \end{array}\right]$$

4-fold symmetry centers

$$4\ (\mathrm{a}):\ 0\,0\,0,\ \frac{1}{2}\,0\,\frac{1}{2},\ \frac{1}{4}\,\frac{1}{2}\,\frac{3}{4},\ \frac{3}{4}\,\frac{1}{2}\,\frac{1}{4}.\qquad (\mathrm{H})$$

$$4\ (\mathrm{b}):\ \frac{1}{2}\,0\,0,\ 0\,0\,\frac{1}{2},\ \frac{1}{4}\,\frac{1}{2}\,\frac{1}{4},\ \frac{3}{4}\,\frac{1}{2}\,\frac{3}{4}.\qquad (\mathrm{Q})$$

$$4\ (\mathrm{c}):\ 0\,\frac{1}{2}\,0,\ \frac{1}{2}\,\frac{1}{2}\,\frac{1}{2},\ \frac{1}{4}\,0\,\frac{3}{4},\ \frac{3}{4}\,0\,\frac{1}{4}.$$

$$4\ (\mathrm{d}):\ \frac{1}{2}\,\frac{1}{2}\,0,\ 0\,\frac{1}{2}\,\frac{1}{2},\ \frac{1}{4}\,0\,\frac{1}{4},\ \frac{3}{4}\,0\,\frac{3}{4}.$$

of averaged molecule $1/2(C_{12}H_{10}O_4)$ lying on two of the centers of symmetry in a lattice of space group $P2_1/n$, and corresponds to the structure given in the first paper of Foz and and Palacios.[3] The orientation of the molecular axes was determined easily by the method of Fourier transform[5] using the reflections (0*k*0) and (00*l*). In calculating this transform, a hypothetical molecular model shown in Fig. 2 was adopted. Atomic parameters thus obtained were refined through repeated $\rho(yz)$ syntheses and structure-factor calculations (0*kl*).

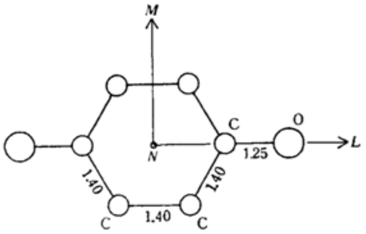

Fig. 2. Molecular model used in calculating the Fourier transform. The weight of the oxygen atom was taken to be 4/3 times that of the carbon. Axis *N* points up and is perpendicular to both *L* and *M*.

The averaged structure obtained here was in striking accordance with that suggested by Banerjee[6] from magnetic data. According to our results, the normal to the averaged molecular plane, when projected upon (010), makes an angle 15.0° with the *a* axis, which accords well with the angle 15.1° between the *a* axis and the direction of maximum susceptibility reported by Banerjee. This fact alone will support Banerjee's view that the crystal of quinhydrone consists of molecules of quinone and hydroquinone.

Determination of *x* and *z* Parameters.—Since there are four $C_{12}H_{10}O_4$ units in the unit cell having eight-fold general positions, two types of structure are possible; one of which consists of two different kinds of molecules, corresponding to quinone and hydroquinone, each lying on one of the four-fold centers of symmetry, say 4(a) and 4(b) (Table I.); and the other consists of only one kind of molecule (semiquinone type) which are situated around (1/4 0 0), etc. Since the former type consisting of quinone and hydroquinone seemed to be more plausible in view of the work of Anderson[1] and that of Banerjee[6], we studied mainly on this line. We also examined the semiquinone type structure, which we shall later mention briefly.

In order to find out how and to what extent these two sorts of component molecule deviate in shape and orientation from the hypothetical averaged molecule, we performed trial-and-error calculations on (*h*0*l*) reflections with *h* and *l* odd, using scaled structure factor maps.

After sufficient agreement was obtained between calculated and observed *F*-values, we prepared an electron density projection $\rho(xz)$ using almost all (*h*0*l*) reflections. Parameters thus found, when combined with $\rho(yz)$ already obtained, led us to a group of structures in which the benzene ring of the hydroquinone molecule was somewhat deformed. Thus we performed two series of extensive trial-and-error calculations in order to be sure whether this deformation was real or not. In one series of the calculation we always assumed a regular hexagon with sides 1.39Å for hydroquinone, while in the other no such assumption was made. The best model we obtained in each of the two series gave the values of reliability indices 0.158 and 0.154 respectively, both including the contribution of hydrogen atoms. The signs of *F*-values calculated from these two models differed only in two weak reflections out of 67 observed values, and the change in $\sum |F(h0l)|$ is only 0.6% if we neglect them. Hence we proceeded to the next stage omitting these two reflections.

The next step was to obtain the final *x* and *z* parameters for all the atoms. To do this we used the method of differential synthesis and applied the corrections for series-termination. This step was repeated twice. Carbon atom C_{IV}, which is linked to oxygen O_{II} to form a quinone molecule, was not resolved in $\rho(xz)$ projection (Fig. 3), so that *x* and *z* parameters for C_{IV} were obtained by least squares calculations treating only these two parameters as variables, after other atoms were all fixed.

The reliability index *R* obtained for *F*(*h*0*l*) was reduced to 0.124 including the contributions of hydrogen atoms.

Determination of *y* Parameters—The determination of *y* parameters was much more troublesome. Although we had obtained by this stage (R=0.139 for (0*kl*) including hydrogen atoms) fairly good parameters for all the atoms from trial-

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[5] G. Knott, *Proc. Phys. Soc.*, **52**, 229 (1940).
[6] S. Banerjee, *Z. Krist.*, **100**, 316 (1939).

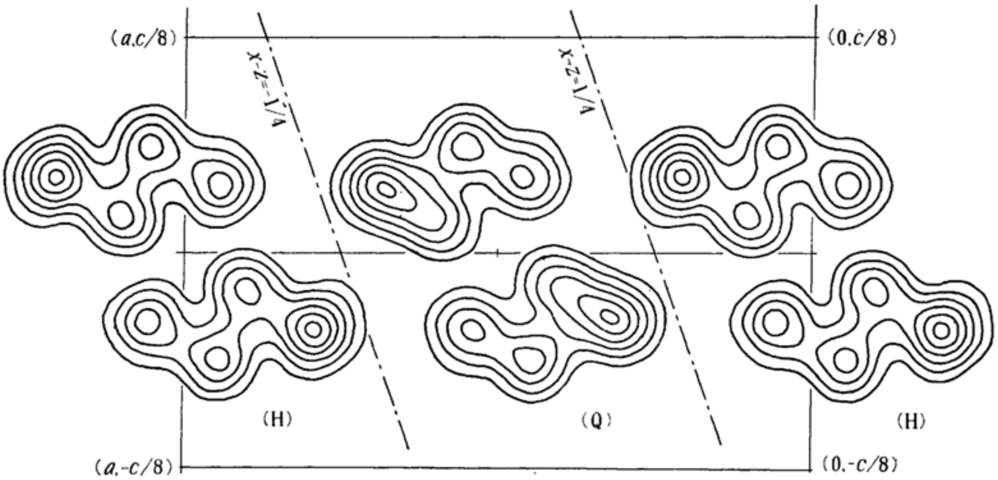

Fig. 3. Electron density projection $\rho(xz)$. Limiting planes for the bounded projections are also indicated by chain lines (see text).

and-error method, the refinement seemed to be hopeless when we used $(0kl)$ reflections only, even by way of least squares calculations, since the component molecules overlap atom to atom almost completely in the projection along [100] (Fig. 4). However, we were able to overcome this difficulty using the method of bounded projection. This method was especially convenient in this structure, because, if we choose suitable limiting planes, we need only (hkl) intensities with h and l odd, which are all weak, and appropriate values for them can be estimated without too much difficulty. Actually, we prepared bounded projections in a modified form so as to separate quinone and hydroquinone completely. The projection was made along [100] axis, with the limiting planes at,

$$x-z=1/4 \text{ and } x-z=-1/4,$$

as indicated in Fig. 3. The expressions for these bounded projections are as follows:

$$B_I=\frac{2a}{V}\sum_{-k}^{k}\sum_{0}^{l}\sum_{-h}^{h}\int_{x=-\frac{1}{4}+z}^{x=\frac{1}{4}+z}F_{hkl}\cos 2\pi(hx+ky+lz)\mathrm{d}x$$

$$=B_0+B_h$$

$$B_{II}=\frac{2a}{V}\sum_{-k}^{k}\sum_{0}^{l}\sum_{-h}^{h}\int_{x=-\frac{1}{4}+z}^{x=\frac{3}{4}+z}F_{hkl}\cos 2\pi(hx+ky+lz)\mathrm{d}x$$

$$=B_0-B_h$$

where

$$B_0=\frac{a}{V}\sum_{-k}^{k}\sum_{0}^{l}F_{0kl}\cos 2\pi(ky+lz)$$

$$B_h=\frac{2a}{V}\sum_{-k}^{k}\sum_{1}^{l}\left[\sum_{\substack{-h\\(h\neq 0)}}^{h}\left(\frac{1}{\pi h}\sin\frac{\pi h}{2}\right)F_{hkl}\right]$$

$$\times\cos 2\pi\{ky+(l+h)z\}$$

The intensities for (hkl) with $h=3$, 1, $\bar{1}$ and $\bar{3}$ collected from oscillation photographs were utilized after the application of necessary corrections. No effort was made to obtain data with h higher than these, as they did not seem to effect the results seriously. Signs of $F(hkl)$ were derived from calculated values using the best set of parameters obtained at that stage, contributions from hydrogen atoms being neglected. The first projection was calculated using x and z parameters which were obtained by differential Fourier syntheses, and the third and last one was calculated only along b axis through the atomic positions, after x and z parameters were all fixed. Termination corrections were also applied. y parameters thus obtained were listed in Table II together with the x and z parameters obtained in the previous section. Calculated and

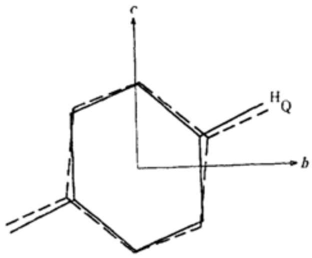

Fig. 4. Projection of the two component molecules along the a axis.
H: hydroquinone, Q: quinone.

TABLE II

FINAL ATOMIC CO-ORDINATES

	x	y	z
C_{I}	0.1039	0.1640	0.0216
C_{II}	0.0518	0.0077	0.0610
C_{III}	0.0549	0.1695	−0.0412
C_{IV}	0.6021	0.1854	0.0195
C_{V}	0.5523	0.0121	0.0621
C_{VI}	0.5439	0.1632	−0.0453
O_{I}	0.2128	0.3355	0.0440
O_{II}	0.6849	0.3496	0.0374

TABLE III

OBSERVED AND CALCULATED F-VALUES FOR ZONAL REFLECTIONS

$0k$ l	$\|F_{obs}\|$	F_{calc}
00. 4	122	142
8	82	−85
12	72	83
16	15	−12
20	6	6
24	3	0
02. 0	32	−37
2	39	41
4	47	−52
6	59	73
8	23	−17
10	16	17
12	26	25
14	39	−41
16	34	33
18	38	−45
20	3	1
22	15	−15
24	15	−13
26	12	10
04. 0	16	−22
2	22	23
4	30	−28
6	32	34
8	10	−8
10	3	3
12	28	24
14	33	33
16	24	26
18	25	27
20	4	−19
22	9	7
24	12	12
06. 0	42	56
2	9	−7
4	22	25
6	11	−11
8	22	−20
10	4	−3
12	22	−22
14	0	1
16	4	−3
01. 2	54	−63
4	37	−45
6	29	−17
8	47	−60
10	13	−5
12	31	−31
14	20	19
16	10	−12
18	15	8
20	7	−4
22	14	−17
24	0	3
26	14	−15
03. 2	13	17
4	13	−14
6	36	−40
8	0	−3
10	35	−33
12	4	−5
14	15	8
16	0	5
18	24	16
20	0	2
22	0	3
24	3	1
05. 2	29	27
4	7	8
6	0	−3
8	17	17
10	5	−10
12	15	17
14	3	4
16	5	6
18	0	3
20	0	−2
07. 2	4	5
4	7	−7
6	8	−5
8	7	−6
10	5	−4
12	4	−4

$h0$ l	$\|F_{obs}\|$	F_{calc}
10. 1	12	−13
5	8	−5
9	9	9
13	12	12
17	2	3
21	5	−5
25	7	−5
20. 2	24	−22
6	92	−85
10	42	−34
14	9	11
18	4	−4
22	19	−14
30. 3	21	21
7	22	21
11	0	0
15	12	−13
19	6	−10
40. 0	0	2
4	21	22
8	13	11
12	5	−6
16	23	−26
20	20	−19
50. 1	8	−8
5	17	−19
9	6	−8
13	9	8
17	10	13
60. 2	37	28
6	8	−11
10	19	18
14	12	13
18	0	−1
70. 3	0	−2
7	9	10
11	10	13
15	4	4
80. 0	21	−24
4	6	5
8	33	36
$\bar{1}0$. 3	5	−1
7	3	−1
11	11	−11
15	10	−10
19	0	−1
23	6	6
$\bar{2}0$. 2	92	79
6	35	39
10	26	32
14	33	31
18	32	26
22	0	3
$\bar{3}0$. 1	0	2
5	8	−7
9	4	−3
13	5	−1
17	5	−4
21	0	−2
$\bar{4}0$. 4	42	−39
8	63	−71
12	25	−24
16	40	42
20	50	48
$\bar{5}0$. 3	7	8
7	11	11
11	10	13
15	0	−1
19	0	0
$\bar{6}0$. 2	8	−4
6	0	5
10	21	−16
14	18	−19
18	2	0
$\bar{7}0$. 1	10	−11
5	8	−8
9	0	1
13	0	4
$\bar{8}0$. 4	16	−16
8	0	2

TABLE IV

OBSERVED AND CALCULATED F-VALUES FOR hkl REFLECTIONS

hk	l	$\|F_{\mathrm{obs}}\|$	F_{calc}
11.	1	6	−4
	3	9	8
	5	7	11
	7	3	0
	9	18	20
	11	10	−10
	13	11	8
	15	12	−10
	17	5	−4
	19	0	−3
	21	9	−8
	23	2	3
	25	5	−4
	27	3	4
12.	1	6	6
	3	10	−12
	5	6	15
	7	17	−18
	9	4	0
	11	5	−5
	13	9	−5
	15	11	9
	17	0	−3
	19	11	11
	21	2	0
	23	2	3
13.	1	3	5
	3	10	−8
	5	0	−1
	7	5	−4
	9	7	−7
	11	8	9
	13	6	−7
	15	15	13
	17	2	−3
	19	10	7
	21	0	0
	23	2	−4
14.	1	0	1
	3	2	−1
	5	2	−2
	7	6	3
	9	7	−7
	11	0	0
	13	6	−4
	15	7	−4
	17	3	4
	19	7	−5
	21	8	7
$\bar{1}1$.	1	5	8
	3	4	3
	5	7	9
	7	2	−3
	9	7	7
	11	2	0
	13	0	1
	15	8	6
	17	5	−4
	19	4	4
	21	3	−4
	23	0	0
	25	2	2
	27	3	−2
$\bar{1}2$.	1	0	2
	3	0	−1
	5	0	0
	7	0	1
	9	0	0
	11	6	6
	13	3	−5
	15	7	6
	17	9	−8
	19	4	3
	21	6	−5
	23	0	−2
$\bar{1}3$.	1	3	−3
	3	0	−2
	5	0	0
	7	0	0
	9	7	−4
	11	2	2
	13	6	−3
	15	0	0
	17	6	4
	19	0	−2
	21	9	7
	23	2	−3
$\bar{1}4$.	1	4	6
	3	0	0
	5	0	0
	7	0	−2
	9	8	−6
	11	0	−2
	13	2	−3
	15	0	−1
	17	3	3
	19	0	0
	21	5	4
15.	1	5	4
	3	0	3
	5	0	2
	7	4	5
	9	4	−3
	11	0	1
	13	0	−1
	15	0	−2
	17	4	4
16.	1	0	0
	3	10	11
	5	0	−2
	7	6	8
	9	0	0
	11	0	2
	13	2	2
	15	0	−1
17.	1	2	−2
	3	6	2
	5	0	1
	7	0	1
	9	0	4
31.	1	10	−13
	3	1	1
	5	13	−13
	7	14	−14
	9	3	−1
	11	11	−12
	13	8	9
	15	3	2
	17	9	8
	19	9	9
	21	3	0
	23	5	4
32.	1	13	−11
	3	9	−9
	5	0	3
	7	12	−14
	9	16	17
	11	5	−6
	13	17	16
	15	6	4
	17	4	3
	19	6	6
	21	8	−7
	23	0	0
$\bar{1}5$.	1	5	−5
	3	2	1
	5	8	−9
	7	2	3
	9	4	−7
	11	0	0
	13	0	−2
	15	2	−2
	17	2	2
$\bar{1}6$.	1	5	−5
	3	2	3
	5	0	3
	7	2	3
	9	4	5
	11	2	−2
	13	5	5
	15	5	−4
$\bar{1}7$.	1	5	5
	3	6	2
	5	8	7
	7	0	0
	9	6	6
$\bar{3}1$.	1	10	−15
	3	0	−2
	5	7	−6
	7	6	5
	9	1	1
	11	0	3
	13	0	−2
	15	5	1
	17	2	−5
	19	2	2
	21	0	−3
	23	5	2
$\bar{3}2$.	1	0	3
	3	13	13
	5	6	7
	7	7	6
	9	3	4
	11	2	1
	13	0	0
	15	0	−1
	17	0	1
	19	2	−3
	21	4	3
	23	6	−4

hk	l	$\lvert F_{obs}\rvert$	F_{calc}
33.	1	12	12
	3	3	− 8
	5	14	14
	7	4	− 8
	9	0	− 1
	11	0	− 2
	13	13	−12
	15	0	4
	17	7	− 8
	19	2	5
	21	0	0
34.	1	8	9
	3	2	− 2
	5	4	2
	7	0	1
	9	10	−10
	11	2	6
	13	9	−11
	15	8	8

hk	l	$\lvert F_{obs}\rvert$	F_{calc}
$\bar{3}3$.	1	1	3
	3	0	− 1
	5	0	0
	7	3	− 5
	9	0	− 1
	11	0	− 1
	13	0	0
	15	0	1
	17	0	1
	19	0	− 1
	21	0	1
$\bar{3}4$.	1	0	− 3
	3	2	− 3
	5	2	− 3
	7	3	5
	9	0	− 3
	11	0	4
	13	0	− 2
	15	0	0

hk	l	$\lvert F_{obs}\rvert$	F_{calc}
34	17	0	− 2
	19	8	5
35.	1	0	4
	3	4	5
	5	0	1
	7	8	8
	9	0	0
	11	7	4
	13	4	2
	15	4	− 3
	17	0	3
36.	1	0	2
	3	4	3
	5	0	− 1
	7	3	4
	9	0	− 2
	11	0	1

hk	l	$\lvert F_{obs}\rvert$	F_{calc}
$\bar{3}4$	17	0	0
	19	0	0
$\bar{3}5$.	1	0	0
	3	0	4
	5	0	2
	7	0	− 1
	9	0	− 1
	11	5	− 6
	13	0	− 1
	15	7	− 6
	17	1	2
$\bar{3}6$.	1	0	− 1
	3	2	− 5
	5	2	− 2
	7	6	− 6
	9	0	0
	11	6	− 6

observed F-values are given in Tables III and IV.

Tests on the Semiquinone-type structure.—Another type of structure consisting of semiquinone-type molecules was also checked by trial calculations followed by differential Fourier syntheses. After two steps of approximations we were able to obtain a parameter set with reliability index $R=0.24$ for $(h0l)$ reflections neglecting the contributions of hydrogen atoms, while that for the correct structure was 0.15. If we devide F-values into groups of even and odd reflections we find for the semiquinone type (excluding hydrogen atoms) $R(\text{even})=0.19$ and $R(\text{odd})=0.55$, as compared with those of the other (excluding hydrogen atoms) $R(\text{even})=0.15$ and $R(\text{odd})=0.16$. The R-value for the reflections with h odd is exceedingly large in the case of semiquinone-type. It may be considered as an indication that the structure of this type is wrong as to the structural features especially responsible for these reflections, that is, as to the deviations from the averaged structure.

Collection of intensity data.—Most of the intensity data were collected from two sets of oscillation photographs about a and b axes. In order to obtain good intensity estimates even for weaker reflections with h and l odd, we prepared, for each range of oscillation, a photograph of very long exposure in addition to a usual one. A rotation photograph was taken about the a axis using multiple-film technique. This provided further confirmation and gave measurable intensities even for very strong reflections. All these data were combined and served for most part of the present work.

During the course of analysis, however, it was found that the specimen showed a strong extinction. Additional sets of oscillation photographs were then prepared for both a and b axes using a tiny crystal dipped into liquid air several times. The disagreement between calculated and observed F-values for strongest reflections became less remarkable, but we were unable to eliminate the effect of extinction completely.

All the photographs were prepared using Cu-K radiations, with or without a nickel filter, and the intensities were estimated by comparing them visually with a series of standard intensity scales, except in measuring rotation photographs where a recording microphotometer was used. The number of reflections actually observed as compared with what were possible is listed below:

type of reflections		number of reflections	
		observed	possible
$0kl$		74	83
$h0l$	h and l even	39	44
	odd	33	42
$1kl$, $\bar{1}kl$ $(k=0)$		100	142
$3kl$, $\bar{3}kl$		73	120

Description and Discussion of the Structure

The structure of quinhydrone obtained here consists of two sorts of molecules, quinone and hydroquinone, of which the latter appears to be deformed to some extent as is shown in Fig. 5. The average plane of six carbon atoms of quinone with its center at 1/4, 0, 0 is given by the equation

$$-0.836(ax-3.837)+0.507by+0.210cz'=0,$$

where the z' axis was taken perpendicular to x and the oxygen O_{II} comes by 0.055Å outside of the plane. The difference between the two C-C(H) bond lengths adjacent to the C=O group is scarcely significant and the mean value 1.465Å is rather short in comparison with 1.50 Å reported for *p*-benzoquinone⁷⁾. This is probably related to the observed elongation of $C_V=C_{VI}'$ bond from the standard value 1.32 Å to 1.335 Å, though the difference is hardly significant. C=O bond length 1.234Å observed is a value commonly found for the carboxyl group forming a hydrogen bond, though somewhat shorter value 1.15Å is reported for *p*-benzoquinone. The average plane containing six carbon atoms of the hydroquinone molecule with its center at the origin is given by

$$-0.811ax+0.542by+0.219\,cz'=0$$

The oxygen atom O_I calculated to be only 0.014Å outside the plane may well be considered to be almost coplanar with the benzene ring. The observed C-O(H) distance 1.409Å is considerably larger than the usual 1.36Å for a phenolic C-O, which may possibly be related to the deformation of the benzenoid ring described below.

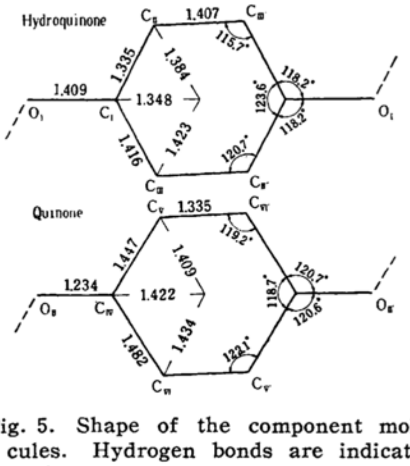

Fig. 5. Shape of the component molecules. Hydrogen bonds are indicated by broken lines.

A rather striking feature is the deformation of the benzenoid ring of the hydroquinone molecule. In fact, the bond length C_I-C_{II} is contracted to 1.335Å, while C_I-C_{III} and $C_{II}-C_{III}'$ are 1.416 and 1.407Å respectively, and they seem to be elongated somewhat. Further, the angle $C_I-C_{III}-C_{II}'$ is found to be 115.7° and as a result of these changes, the benzenoid ring rather resembles a quinoid ring. Although the cause of this deformation is not yet clear, it will be interesting to add here that the C_I-C_{II} bond, which appears shorter than C_I-C_{III}, is nearly parallel to the hydrogen bond O-H⋯O which will be described in the next paragraph. A similar deformation was also reported in the case of 1, 4-dimethoxybenzene (Fig. 6) by Robertson and others⁸⁾ although they did not try to explain it. We may mention in this connection that Tomiie⁹⁾ pointed out once that the lone-pair electrons at the oxygen atom may possibly influence the benzenoid ring to stabilize one of the resonance forms.

Fig. 6. Shape of 1, 4-dimethoxybenzene after Robertson.

The two sorts of molecules, quinone and hydroquinone, are linked alternately through O-H⋯O hydrogen bonds of moderate length (2.71Å) to form a zigzag chain which is extended throughout the crystal*. Fig. 7 (a) is a part of the structure at $z=0$ and shows that these chains are running along [120]. Planes of molecules of the same sort are all parallel within a single chain, since they correspond to some translation of the crystal lattice, while those of one sort are tilted slightly (about 2°30′) with respect to those of the other. Fig. 7 (b) shows a part of the similar sheet at $z=1/4$, but in this case, the chains are seen to be running along [$\bar{1}$20]

Fig. 7 (a) also shows how these chains are stacked side by side to form a molecular sheet parallel to (001). These sheets are again piled up into a sort of layer lattice. A perspective view of a part of the structure is given in Fig. 8.

Between the neighboring sheets, the nearest approach distances are those between non-bonded carbon and oxygen atoms of lengths 3.31∼3.83Å as shown in Fig. 8. These values are comparable with 3.4Å reported by Robertson in *p*-benzoquinone⁷⁾

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7) J. M. Robertson, *Proc. Roy. Soc.*, **A150**, 106 (1953).

8) T. H. Goodwin, M. Przybylska and J. M. Robertson, *Acta Cryst.*, **3**, 279 (1950).

9) Y. Tomiie, informal discussion.

* Such a chain-like structure is often accompanied by marked thermal motion of the molecular plane, which was actually observed in the present case as strong diffuse scattering on both Laue and oscillation photographs.

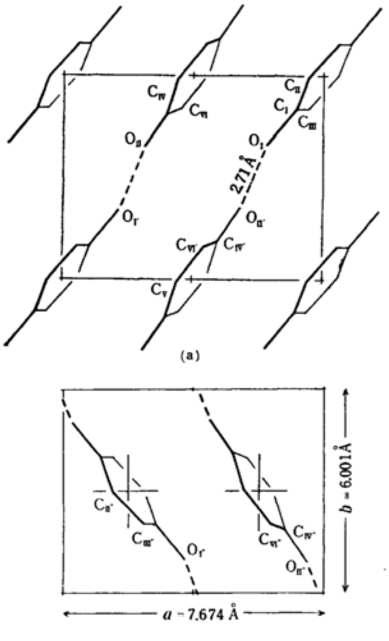

Fig. 7. Part of the molecular sheet at $z=0$ (a) and $z=1/4$ (b).

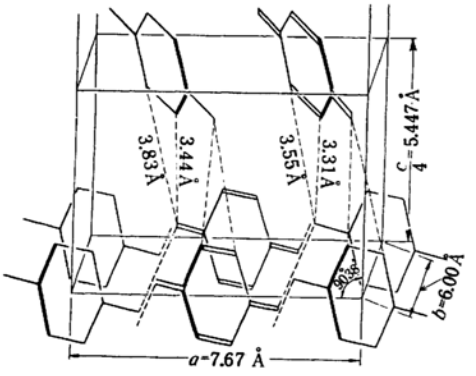

Fig. 8. Perspective view of a part of the structure of quinhydrone.

and with 3.24 and 3.39Å given by Abrahams in *p*-dinitrobenzene.[10] Similar values are often found between aromatic carbon and oxygen atoms and do not seem to be exceptionally short. Only it will be interesting to notice here that the oxygen atom of one sort of molecule always has the carbon atoms of the other as its neighbors. No C···C or O···O distances are shorter than 4Å between the neighboring sheets.

Hitherto we have seen that the crystal of quinhydrone is a sort of layer structure containing hydrogen bonds. Suzuki and Seki[11] determined the heat of formation of crystalline quinhydrone and estimated that the hydrogen-bond energy seems to contribute to a considerable part to it. But the remarkably compact structure, suggested by the observed density 1.401 in comparison with those of hydroquinone 1.33 and quinone 1.32, and the characteristic coloring of quinhydrone are not explained by hydrogen bonds.

Another type of interaction also seems to be taking place within the molecular sheet. We have already mentioned that the two component molecules are piled up alternately along the *a* axis, and overlap atom to atom almost completely when projected along this axis (Fig. 4). The planes of adjacent molecules are nearly parallel (inclination about 2°30′) and the perpendicular distance between the averaged molecular plane is measured to be 3.16Å. This value is remarkably short for an interplanar distance of aromatic molecules which is usually found to be larger than 3.4Å and may not have been realized without a considerable attraction between these molecules, if the repulsive forces are assumed to be the same. We may thus consider that these component molecules are linked in some way along the *a* axis and make up a sort of molecular column of alternating quinone and hydroquinone molecules along this direction. Or we may even look upon the structure of quinhydrone as consisting of such columns linked side by side through hydrogen bonds to form a sheet. Similar columns are also found in the molecular compound analyzed by Powell et al.[2] which does not contain hydrogen bonds. So that the existence of such columns may be looked upon to be a characteristic feature of these types of molecular compounds.

Now let us look into the detailed structure of the molecular column in quinhydrone. Fig. 9 is the projection of two

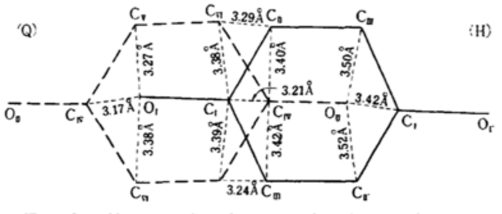

Fig 9. Perpendicular projection of two neighboring molecules within a column.

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[10] S. C. Abrahams, *Acta Cryst.*, **3**, 194 (1950); F. J. Llwellyn, *J. Chem. Soc.*, **1947**, 884.

[11] K. Suzuki and S. Seki, This Bulletin, **26**, 372 (1953).

succeeding molecules within a column upon the mean molecular plane and shows the relative positions of the stacking molecule more clearly. Here, it must be born in mind that each molecule lies on the center of symmetry, so that each component molecule is sandwiched between molecules of the other component on both sides. Atomic distances between the molecules are also given in the figure. C···O distances found here are not very different from those between the molecular sheets. But the intermolecular C···C distances so short as those given here do not seem to have been reported before except in 3:4-benzophenanthrene.[12]

Nakamoto[13] investigated the optical dichroism of quinhydrone and some other molecular compounds of similar type and concluded that, in these substances, π-electrons are more mobile in the direction perpendicular to the plane than in the plane of the molecule, contrary to the case of ordinary aromatic compounds, where π-electrons are more mobile along the molecular plane. This result, as was pointed out by himself, will be explained qualitatively if we assume that the characteristic absorption in quinhydrone is due to a stable complex which is made up from quinone and hydroquinone through the mechanism of charge-transfer proposed by Mulliken.[14] Also the observed short intermolecular distance will be explained by this concept.

But why, then, is an unusually stable complex formed in the case of quinhydrone? A theoretical treatment by Suzuki[15] seems to answer the essential points of this question. He extended the treatment of Mulliken to the case of an infinite chain and calculated the electronic state of quinhydrone to the Bloch approximation and concluded that in the excited state most of the mobile electrons are transferred from hydroquinone to quinone molecule, so that the observed spectra (maximum approximately at 550 and 380 mμ) correspond to the intermolecular charge-transfer spectra. In other words, he concludes that the attraction between the two components in quinhydrone may be due to the interaction between the highest occupied molecular orbital level of hydroquinone and the lowest unoccupied one of the quinone molecule, and that the very strong interaction in this case may probably be attributed to the fact that the molecular orbitals of quinone and hydroquinone have the same symmetry and, at the same time, their energy difference is small.

Thus, we have in quinhydrone a remarkable example of a series of molecular compounds of which combined investigations of the crystal structure and of physical properties seem to be worth performing.

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[12] F. H. Herbstein and G. M. Schmidt, *J. Chem. Soc.*, **1954**, 3302.

[13] K. Nakamoto, *J. Am. Chem. Soc.*, **74**, 1739 (1952).

[14] R. S. Mulliken, ibid., **74**, 811 (1952).

[15] K. Suzuki, *Busseironkenkyu*, No. **102**, p. 5 (1956), (in Japanese).