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The Crystal Structure of the 1:2 Molecular Complex of Phloroglucinol (1,3,5-Trihydroxybenzene) and *p*-Benzoquinone

BY TOSIO SAKURAI AND HIROYUKI TAGAWA*
The Institute of Physical and Chemical Research, Rikagaku Kenkyusho, Yamatomachi, Saitama, Japan

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The crystal structure of the 1:2 molecular complex of phloroglucinol and *p*-benzoquinone (1,3,5-$C_6H_3(OH)_3:(C_6H_4O_2)_2$) has been determined. The crystal is triclinic, space group $P\bar{1}$, with $a=9{\cdot}716$, $b=10{\cdot}589$, $c=8{\cdot}434$ Å, $\alpha=88°39'$, $\beta=101°44'$. $\gamma=69°46'$, $Z=2$. The crystal consists of a planar array of molecules which are connected by the hydrogen bond to form a zigzag chain. Although the asymmetric unit contains two formula units of *p*-benzoquinone, there are three crystallographically different quinone molecules. Thus, the structural unit may be written as $C_6H_3(OH)_3:C_6H_4O_2:(C_3H_2O)_2$.

Introduction

This paper is the fourth report in a series of crystal-structure analysis of the charge-transfer complexes between *p*-benzoquinone (electron acceptor) and hydroxybenzenes (electron donors) (Sakurai, 1965; Sakurai, 1968; Ito, Minobe & Sakurai, 1970).

Phloroglucinol (1,3,5-trihydroxybenzene) is known to form a 1:2 molecular complex with *p*-benzoquinone (Michaelis & Granick, 1944). A preliminary study of the crystal structure was reported by Sakurai & Tagawa (1968). Unfortunately, due to an error in the cell-constant measurement, the molecular ratio was regarded as 2:1 in that report, instead of 1:2, and the true structure was not obtained. X-ray diffraction data were remeasured after that report, and the correct structure has now been deduced. An interesting feature of this structure is the existence of three crystallographically different quinone molecules, in spite of the two formula units in the asymmetric unit.

Crystal data

Triclinic $P\bar{1}$ (C_i^1)
$a=9{\cdot}716\pm0{\cdot}026$, $b=10{\cdot}589\pm0{\cdot}017$,
$c=8{\cdot}434\pm0{\cdot}018$ Å,
$\alpha=88°39'\pm8'$, $\beta=101°44'\pm13'$, $\gamma=69°46'\pm11'$,
$V=793{\cdot}0\pm2{\cdot}8$ Å^3.
Formula: $C_6H_3(OH)_3:(C_6H_4O_2)_2$. F.W. 342.
$D_m=1{\cdot}433$ g.cm^{-3}, $D_x=1{\cdot}433$ g.cm^{-3}, $Z=2$.

Experimental

Single crystals, of dark-orange colour, were obtained from the mixture of the solution of the component molecules. The growth condition is very sensitive to the molar ratio, temperature, evaporating rate and humidity. The best crystals were obtained as follows: 1·5g of *p*-benzoquinone (0·014 mole) was dissolved in 12 ml of acetone, and 1·0g of phloroglucinol dihydrate (0·0062 mole) was dissolved in 2 ml of acetone. Both solutions were poured into a 200-ml beaker. After 12 minutes, 2 ml of benzene were added to the mixture. The beaker, covered with 4 sheets of gauze and a piece of filter paper for qualitative analysis, was left in a room at a temperature of 20 °C ± 1 and humidity 42% ± 2. Single crystals were obtained within 24 hours. Generally, the quality of the crystals was not as good as that of other quinhydrone-type complexes so far studied. A rod-shaped crystal elongated along the [1 0 3] axis was sealed in a glass capillary, and 893 independent X-ray diffraction intensities were measured

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* Present address: Department of Engineering Chemistry, Nihon University, Kanda Tokyo, Japan.

with a single-crystal diffractometer *RIKEN READ*1 (Sakurai, Ito & Iimura, 1970) with monochromatized Mo $K\alpha$ radiation. Wilson's statistics revealed that the structure has a centre of symmetry.

Structure determination

First, the unitary structure factors were calculated. The largest one $U(\bar{3},\bar{1},1)$ is almost 1·0, which indicates that the molecule is parallel to the $(\bar{3},\bar{1},1)$ plane. Then a new coordinate system $\mathbf{a}'$, $\mathbf{b}'$, $\mathbf{c}'$ was selected so that $\mathbf{b}'$ and $\mathbf{c}'$ were on the molecular plane. The relation between the primed system and the original coordinate system is:

$$\begin{aligned} \mathbf{a}' &= \phantom{-\mathbf{a}+{}} \mathbf{b} \\ \mathbf{b}' &= -\mathbf{a} + 2\mathbf{b} - \mathbf{c} \\ \mathbf{c}' &= \phantom{-\mathbf{a}+2{}} \mathbf{b} + \mathbf{c} \end{aligned}$$

and the cell constants are:

$$a' = 10{\cdot}59,\ b' = 20{\cdot}74,\ c' = 13{\cdot}69\ \text{Å},$$
$$\alpha' = 61{\cdot}3,\ \beta' = 38{\cdot}0,\ \gamma' = 31{\cdot}8°.$$

In this system, since the molecular plane is on the $\mathbf{b}'\mathbf{c}'$ plane, $U(h',k',l')$ with fixed indices k' and l' have nearly the same value, independent of h'. Therefore, the mean value

$$V(k',l') = \sum_{h'} U(h',k',l')/H,$$

where H is the total number of $U(h',k',l')$ in the summation, was calculated, and a two-dimensional Patterson function with coefficients $V(k',l')$ was calculated along the $\mathbf{b}'\ \mathbf{c}'$ plane (Sakurai & Tagawa, 1968). This is shown in Fig. 1.

The characteristic features of this Patterson function are as follows:

Table 1. *Observed and calculated structure factors*

H	FO	FC
H 0 0		
1	10	-9
2	7	-5
3	38	37
4	7	7
5	17	-17
6	15	-13
7	3	2
8	4	3
H 1 0		
-8	5	1
-3	15	-16
-2	10	-10
-1	3	3
0	3	-2
1	8	-8
2	3	2
3	6	5
4	3	-2
5	6	6
7	4	-2
8	6	-6
9	7	-3
H 2 0		
-7	4	-2
-5	10	10
-2	36	-35
-1	18	19
0	32	-33
1	69	74
2	4	1
3	19	20
4	30	33
5	4	-3
6	7	8
7	8	-7
8	5	-3
9	4	-2
H 3 0		
-7	4	5
-6	5	4
-5	3	-1
-2	8	9
-1	2	-3
0	22	21
1	31	30
2	5	-5
3	34	-37
4	11	-11
5	9	8
6	9	10
7	3	-5
8	7	6
9	5	4
H 4 0		
-6	5	4
-5	4	-3
-3	2	-3
-2	13	12
-1	45	-41
0	8	-5
1	30	29
2	44	-44
3	5	-4
4	15	-13
5	4	-5
6	4	-1
7	4	0
8	19	-18
H 5 0		
-4	11	11
-2	24	-25
-1	13	-14
0	11	11
1	10	11
2	7	-9
3	17	16
4	13	15
6	8	-7
7	3	2
8	5	-5
H 6 0		
-5	6	6
-4	6	4
-2	8	9
0	19	-14
1	15	-17
2	14	14
3	43	-40
6	6	6
9	9	-8
H 7 0		
-4	6	2
-3	4	-1
-1	7	7
0	3	5
1	9	-9
2	3	-3
5	7	-8
6	8	8
7	2	2
8	4	-3
H 8 0		
-3	7	7
-1	3	-2
0	5	-4
4	3	-3
5	4	2
6	7	-7
7	11	11
H 9 0		
-1	5	-2
0	8	-6
4	4	0
6	4	2
H 10 0		
2	20	-20
3	4	-1
4	5	3
H-10 1		
-3	6	-5
H -9 1		
-6	4	0
-3	4	0
-2	2	0
-1	13	-16
0	6	7
1	4	-8
H -8 1		
-8	3	-4
-5	3	-1
1	4	7
H -7 1		
-6	16	-16
-5	3	2
-4	4	-6
-3	10	-9
-2	8	-9
-1	2	3
1	9	9
2	3	4
3	21	21
H -6 1		
-7	3	5
-6	9	11
-5	7	-8
-3	8	8
-2	14	-14
-1	24	-27
0	2	-2
1	12	14
3	3	0
4	2	0
H -5 1		
-7	7	-6
-5	23	-24
-3	6	-4
-2	37	-35
-1	19	18
1	11	-10
2	5	-6
3	10	10
4	16	17
5	3	-5
H -4 1		
-8	3	3
-5	3	3
-4	9	10
-3	16	14
-2	12	11
-1	5	-3
0	4	2
1	3	-3
2	3	2
5	4	-3
H -3 1		
-9	3	2
-7	8	8
-6	10	12
-5	2	0
-4	15	16
-3	17	-18
-2	19	20
-1	52	-52
2	31	26
3	4	-3
5	10	-7
6	3	3
7	3	-5
H -2 1		
-8	5	2
-7	3	-1
-6	3	3
-5	2	-2
-4	9	-9
-3	35	35
-1	8	-9
0	10	-12
1	3	-3
2	3	-3
6	6	6
H -1 1		
-9	5	-6
-8	6	-6
-7	3	0
-6	16	16
-5	2	-1
-4	8	-8
-3	200	201
-2	2	2
-1	3	-5
0	48	52
1	18	17
2	29	-32
3	25	-22
5	8	8
6	23	-22
7	4	3
H 0 1		
-8	3	2
-7	3	-3
-6	11	-12
-5	3	-4
-4	5	3
-3	45	-43
-2	10	8
-1	13	12
2	15	18
3	15	16
4	11	-11
5	22	-24
6	8	-7
8	5	1
H 1 1		
-5	9	-9
-4	4	5
-3	24	-25
-2	96	97
-1	3	2
0	8	8
1	73	80
2	3	1
3	13	16
4	12	-12
5	6	-6
6	6	-5
7	7	-6
H 2 1		
-7	4	-2
-6	3	3
-5	7	8
-4	9	-9
-3	14	15
-2	25	23
-1	12	-13
0	54	-58
1	28	-30
2	21	19
3	15	15
5	9	10
6.	8	9
H 3 1		
-5	2	3
-4	24	-24
-3	4	-2
-2	17	18
-1	39	-36
1	13	-13
2	7	-2
3	13	-15
4	9	9
5	43	-44
6	3	3
8	4	-1
H 4 1		
-5	11	-11
-4	3	-4.
-3	4	3
-2	4	6
-1	4	4
0	10	10
1	24	22
3	15	-14
4	3	4
6	5	-5
9	5	5
H 5 1		
-5	7	8
-3	18	-15
-2	17	-19
-1	20	20
0	59	-57
1	12	-12
2	9	-8
3	21	19
5	3	4
6	25	-24
H 6 1		
-4	3	2
-2	2	-5
1	8	-7
2	8	-10
3	9	9
4	7	7
5	8	-5
6	7	-6
7	3	1
H 7 1		
-4	3	-2
-3	3	-3
-2	7	5
1	11	-10
3	13	-13
4	7	10
5	4	-3
H 8 1		
-3	5	-4
3	6	4
4	5	5
H 9 1		
-1	17	-19
5	22	23
7	12	-13
H 10 1		
1	6	-8
2	4	-5
4	4	4
H-10 2		
-4	9	-13
-3	4	4
H -9 2		
-5	3	5
-4	4	4
-3	4	-5
0	4	-7
H -8 2		
-5	6	-8
-4	4	-2
-3	3	-1
-2	9	10
H -7 2		
-8	3	-3
-7	4	4
-6	2	3
-5	7	-7
-3	2	-3
-1	5	7
1	4	2
2	5	4
3	3	-4
H -6 2		
-9	3	-1
-8	9	-10
-7	6	5
-5	22	-18
-4	11	12
-3	3	-3
-1	6	-6
0	10	12
1	21	22
2	6	-7
3	8	8
4	39	40
H -5 2		
-8	6	5
-5	14	13
-3	2	-4
-2	3	2
-1	9	8
3	3	0
H -4 2		
-9	3	4
-5	8	8
-4	31	-33
-3	2	-4
-2	2	2
-1	32	26
0	6	-5
2	9	-7
3	4	6
4	9	-9
5	17	16
6	4	-3
H -3 2		
-9	3	1
-7	4	-3
-6	24	25
-3	4	-4
-2	7	-2
-1	16	-15
1	2	4
2	10	10
3	2	1
4	6	8
5	8	9
H -2 2		
-9	6	6
-8	3	1
-7	4	-4
-6	68	67
-5	7	7
-4	3	0
-3	24	26
-2	15	14
-1	24	-25
0	21	-18
1	7	-4
2	8	8
3	45	-41
4	6	5
5	3	3
6	7	-8
H -1 2		
-9	6	-7
-8	2	0
-6	34	-33
-5	14	13
-4	11	11
-3	2	-3
-2	5	6
-1	23	26
0	27	29
1	19	-20
2	48	-50
3	13	-11
4	9	11
H 0 2		
-6	9	-9
-5	57	56
-3	8	-7
-2	74	75
-1	14	13
1	15	-11
3	8	-8
4	19	-18
5	4	-3
7	13	-13
8	4	3
H 1 2		
-7	5	-5
-6	6	6
-5	2	2
-4	6	-7
-3	35	-37
-2	35	-38
-1	24	23
0	14	13
1	3	0
2	8	9
3	15	16
4	6	-6
5	6	-7
8	5	-4
H 2 2		
-7	9	-10
-5	3	4
-4	13	-10
-3	10	11
-2	3	-3
-1	5	4
0	26	-29
1	21	21
2	77	-74
3	6	-5
4	6	-5
5	8	8
7	4	2
H 3 2		
-4	10	11
-3	3	0
-2	13	13
-1	2	-2
0	9	-6
2	6	3
3	20	-18
4	2	-4
5	11	11
6	8	7
7	2	-1
H 4 2		
-6	11	-11
-5	11	-11
-4	13	13
-3	41	-42
-2	16	-17
0	30	27
1	2	-2
2	7	8
3	52	-50
5	4	-5
6	26	-25
8	4	4
H 5 2		
-6	2	4
-5	4	-2
-4	4	-4
-3	6	4
-2	6	-7
-1	3	-4
0	2	2
6	2	-1
H 6 2		
-2	12	-13
0	15	-16
2	6	-2
3	2	3
4	9	12
6	11	12
7	3	-5
H 7 2		
-4	4	-4
-1	2	2
0	5	4
1	8	7
2	5	4
3	11	-12
4	10	-10
7	4	-4
H 8 2		
-3	2	-3
2	28	28
3	7	7
4	22	-22
5	34	36
6	3	-1
H 9 2		
-1	6	-6
1	3	3
3	6	6
4	11	12
5	4	3
6	5	-5
H 10 2		
2	3	3
4	5	5
H -8 3		
-6	3	-3
-4	4	7
-2	4	3
H -7 3		
-7	4	3
-5	9	-8
-4	3	-3
-3	7	7
-2	20	20
-1	5	-5
0	11	8
1	51	49
H -6 3		
-8	8	9
-7	8	-7
-5	3	3
-4	8	7
-3	8	-6
-2	6	-7
1	12	-11
2	9	6
H -5 3		
-7	14	-13
-4	9	9
-3	3	-2
-1	2	0
1	11	-9
2	32	32
H -4 3		
-5	5	-3
-4	13	-12
-2	3	3
-1	13	12
0	5	-6
1	13	14
2	10	10
4	12	-13
H -3 3		
-8	5	6
-6	7	10
-5	5	5
-4	6	-7
-3	8	-6
-2	13	-10
0	46	-44
1	7	6
H -2 3		
-8	8	9
-7	6	5
-6	4	-5
-5	6	7
-4	17	17
-3	21	19
-1	48	-48
0	6	-8
1	8	10
6	5	-4
H -1 3		
-8	24	24
-6	8	-8
-5	38	36
-4	14	12
-3	3	3
-1	12	15
1	43	-40
2	8	-10
3	9	8
4	34	-33
5	2	2
H 0 3		
-8	7	-7
-6	9	-11
-5	25	-24
-4	12	12
-3	6	7
-2	8	6
1	10	-8
2	3	-7
3	2	5
5	4	-9
6	3	-2
H 1 3		
-8	2	0
-6	6	7
-3	18	-19
-2	18	17
-1	63	-62
0	22	-18
2	30	24
3	2	2
7	4	-5
H 2 3		
-7	7	7
-6	5	-3
-4	3	-2
-2	4	-5
-1	16	12
0	31	-25
2	10	11
3	7	4
6	3	6
7	3	3
H 3 3		
-7	6	4
-6	18	-20
-5	10	-10
-3	16	16
-1	8	10
2	12	-14
3	46	-42
5	8	8
6	2	5
H 4 3		
-6	7	7
-5	4	-4
-3	3	-2
-1	2	-3
0	7	8
1	9	1
3	14	16
5	9	-10
6	4	-2
7	3	4
H 5 3		
-5	9	-10
-3	10	-11
-1	5	-1
0	5	3
2	4	-6
3	22	23
4	14	-13
H 6 3		
-3	5	3
-2	8	7
-1	8	7
0	14	-13
1	20	-22
2	5	7

Table 1 (*cont.*)

H	FO	FC
3	5	-2
4	6	-7
H	7	3
-3	2	1
-1	20	22
0	14	14
1	22	-20
2	42	45
3	4	-3
H	8	3
-1	6	-6
0	6	5
1	19	19
2	6	-4
4	4	3
5	3	-1
H	9	3
2	14	-12
3	31	29
H	-8	4
-5	13	13
-3	6	5
-2	39	39
H	-7	4
-7	4	2
-6	3	-4
-5	8	-9
-4	3	3
-3	3	-2
-2	22	-19
-1	16	14
0	3	2
H	-6	4
-2	5	-3
-1	38	38
0	11	-11
2	7	5
H	-5	4
-7	5	-4
-4	6	5
-3	7	-6
-2	12	10
1	17	-19
2	3	-5
3	6	6
H	-4	4
-6	2	-1
-5	8	-7
-4	5	-6
-3	24	-24
-2	2	3
-1	5	0
1	3	4
3	2	-4
H	-3	4
-8	5	6
-7	9	6
-6	2	6
-5	4	-8
-4	21	-23
-3	4	-1
0	13	9
1	2	-2
2	2	5
3	6	-5
H	-2	4
-8	15	15
-7	6	7
-4	12	13
-2	44	-40
-1	8	-13
0	11	11
1	48	-47
2	3	-2
3	2	0
H	-1	4
-8	13	-13
-5	5	4
-4	3	-6
-2	2	-1
-1	4	-1
0	7	4
1	9	9
2	17	-15
H	0	4
-8	2	1
-6	5	-6
-5	6	6
-4	25	-24
-3	18	-16
-2	5	-3
-1	28	22
2	11	-11
3	10	10
5	3	11
H	1	4
-5	4	-4
-4	9	9
-3	19	-16
-2	3	-1
0	2	-3
3	3	6
4	8	10
H	2	4
-6	3	4
-5	2	-2
-4	4	6
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-2	5	-3
-1	13	-15
0	43	-39
H	3	4
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-2	13	1
-1	3	1
0	33	34
1	5	-2
2	20	-21
4	9	9
H	4	4
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-2	5	-4
-1	3	-4
0	21	20
1	25	-22
2	4	1
3	5	-4
6	3	-2
H	5	4
-5	3	3
-3	7	-8
-2	17	-20
-1	11	14
0	5	-7
2	2	5
3	8	10
4	3	0
H	6	4
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-2	9	-9
-1	32	35
0	4	-3
1	4	4
H	7	4
-2	17	18
-1	14	-13
0	3	1
1	6	5
3	10	-12
4	8	-8
H	8	4
-1	14	-13
0	36	36
1	12	10
3	14	13
4	6	5
H	-7	5
-4	29	28
-3	9	-8
H	-6	5
-5	5	3
-4	8	-5
-3	4	4
-2	12	-15
-1	6	-7
0	5	8
H	-5	5
-7	4	-4
-3	4	8
0	4	-5
H	-4	5
-7	5	-7
-3	11	9
-2	5	-6
0	4	-3
H	-3	5
-7	6	6
-5	23	-22
-4	7	-8
-3	5	5
-2	36	-36
-1	8	-7
3	3	2
H	-2	5
-3	9	3
-2	15	14
-1	16	-17
H	-1	5
-7	5	-5
-4	6	7
-2	4	3
-1	16	-16
0	9	10
3	2	4
4	6	7
H	0	5
-7	4	4
-4	7	-5
3	2	3
4	12	-14
5	12	-11
H	1	5
-7	3	3
-5	5	-6
-3	20	-18
-2	6	-5
2	2	4
4	3	-1
5	5	-7
H	2	5
-5	8	3
-3	28	28
-2	7	-4
-1	22	-22
0	11	-12
1	12	12
4	14	12
5	10	10
H	3	5
-5	4	-7
-3	8	7
-2	22	-19
0	3	-1
1	3	-2
2	2	-5
4	9	8
H	4	5
-5	7	-9
-4	6	12
-3	5	-8
-2	5	6
0	9	9
1	3	0
4	4	5
5	3	-6
H	5	5
-4	14	16
-3	3	0
-2	8	6
-1	3	-7
0	3	-4
1	6	-1
2	3	2
4	4	7
H	6	5
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-2	5	4
0	7	-10
1	4	-7
4	3	-4
H	7	5
-1	4	-1
0	16	15
1	11	9
H	-5	6
-5	5	-4
0	9	6
H	-4	6
-5	16	-17
-4	6	-6
-2	2	5
H	-3	6
-5	12	12
-4	10	-11
2	3	-5
H	-2	6
-5	4	2
-4	11	-11
-1	6	7
0	5	5
2	8	-10
H	-1	6
-7	3	-1
-4	8	7
-3	5	-3
-1	6	6
0	3	3
2	12	-14
3	3	5
H	0	6
-5	5	-6
0	33	36
1	11	10
2	2	-4
3	27	28
H	1	6
-6	13	14
-5	4	-3
-4	11	-12
-3	6	-9
0	7	-8
2	15	15
H	2	6
-5	11	-11
-1	7	-5
1	11	11
4	40	39
H	3	6
-5	8	7
-3	2	2
-2	2	1
0	2	4
H	4	6
-4	4	-7
-3	5	-6
-2	3	-1
-1	4	2
3	2	6
H	5	6
-2	3	-4
3	2	0
H	6	6
-1	4	-3
H	-4	7
-4	3	-2
-2	3	11
H	-3	7
-5	3	0
-4	2	2
-2	3	1
-1	9	-12
H	-2	7
-1	7	-9
H	-1	7
-3	20	22
-2	16	16
0	18	19
H	0	7
-2	12	12
-1	13	13
0	26	-25
H	1	7
-2	10	10
0	8	-9
1	47	45
H	2	7
0	11	10
1	16	-13
H	3	7
1	12	-13
H	4	7
-1	4	8

(*a*) Very high peaks appear at the multiple of $y'=\frac{1}{3}$ and $z'=\frac{1}{2}$.
(*b*) Arrangement of peaks around the origin is similar to subsidiary peaks around the high peaks mentioned in (*a*).
(*c*) Six peaks appear at about 1·4 Å from the origin.
(*d*) Six peaks appear at about 2·5 Å from the origin.

(*a*) and (*b*) indicate that this structure consists of a subcell $b_s=\frac{1}{3}\,b'$ and $c_s=\frac{1}{2}\,c'$. This means that the orientations of the six-membered aromatic rings of all molecules are almost the same. The mean orientation of the rings was easily determined from (*c*). Since the subcell structure consists of the superposition of the quinone and phloroglucinol molecules, it was analysed by a hypothetical molecule as shown in Fig. 2(*a*). The weights W of oxygen atoms were treated as parameters. After a few trials, the best weights obtained were $W_1=4/7$, $W_2=1/7$ and $W_3=2/7$. These weights are consistent with the distribution of the Patterson peaks mentioned in (*d*), and the resultant R value for the subcell structure is 19 %.

These values are easily explained by the superposition of the four orientational types of molecules in Fig. 2(*b*), with one molecule of type (1), three of type (2), one of type (3), and one of type (4). If the centrosymmetry is assumed for the original cell, the molecule of type (1) and one of type (2) are at the centers of symmetry, and others are at general positions. From this evidence, and some consideration about hydrogen bonding and the donor acceptor superposition, a satisfactory trial structure [Fig. 2(*c*)] was deduced. This structure was successfully refined by the block-diagonal least-squares method, with anisotropic temperature factors. The final R value for all the observed reflexions is 12·1 %. Structure factors are shown in Table 1 and atomic coordinates are in Table 2. For the convenience of reference, these coordinates are given with respect to the primed coordinate system $\mathbf{a}'$, $\mathbf{b}'$ and $\mathbf{c}'$. Temperature factors are not given in Table 2 because they have little significance in the present state of accuracy.

Table 2. *Atomic coordinates with respect to primed system* ($\times 10^4$)

	x'/a'	y'/b'	z'/c'
O(I, 1)	−384	1032	984
C(I, 1)	−333	903	−690
C(I, 2)	−120	545	447
C(I, 3)	296	−393	1105
O(II, 1)	511	1302	3540
C(II, 1)	221	686	4250
C(II, 2)	624	263	5274
C(II, 3)	509	−435	5956
O(III, 1)	−308	1949	6683
O(III, 2)	−329	4844	3837
C(III, 1)	−589	4248	4614
C(III, 2)	−179	3853	5668
C(III, 3)	−209	3129	6461
C(III, 4)	−415	2683	6037
C(III, 5)	−1025	3121	5105
C(III, 6)	−799	3788	4264
O(IV, 1)	559	4670	−1659
O(IV, 2)	918	2619	1892
O(IV, 3)	−676	2635	−569
C(IV, 1)	444	3986	−961
C(IV, 2)	674	3689	138
C(IV, 3)	734	2924	808
C(IV, 4)	100	2577	684
C(IV, 5)	−300	2989	−284
C(IV, 6)	−183	3684	−1096

Mean standard deviations of coordinates are
0·015 Å for carbon and 0·011 Å for oxygen.

Discussion of the structure

The arrangement of the molecules on the **b**′ **c**′ plane is shown in Fig. 3. The molecular sheet consists of the big zigzag chains connected by the hydrogen bonds. The chain axis extends along the **c**′ direction. The structural unit is shown in Fig. 4. Although the asymmetric unit contains two formula units of *p*-benzoquinone, there are three crystallographically different quinone molecules, (I), (II) and (III). Therefore, the structural unit should be written as $C_6H_3(OH)_3$:$C_6H_4O_2$:$(C_3H_2O)_2$. Molecules (I) and (II) have a center of symmetry, and are in the skeleton of the zigzag chain. Molecule (III) is pushed outward from the chain, and has a free carbonyl end. The neighbouring chains are interlocked through molecule (III).

The intramolecular bond distances and angles are shown in Fig. 4. Although there are some irregularities of lengths and angles, perhaps due to the poor nature of the crystals used in collecting the intensity data, the mean bond lengths and angles are similar to those reported for the individual molecules; quinone by Trotter (1960), phloroglucinol by Maartman-Moe (1965).

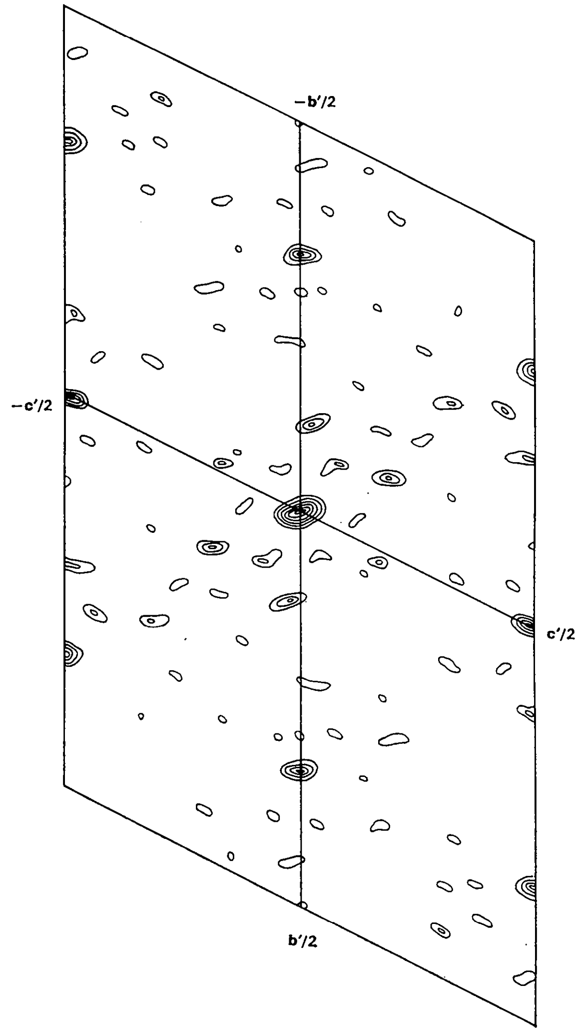


Fig. 1. A modified Patterson function along the molecular plane **b**′ **c**′.

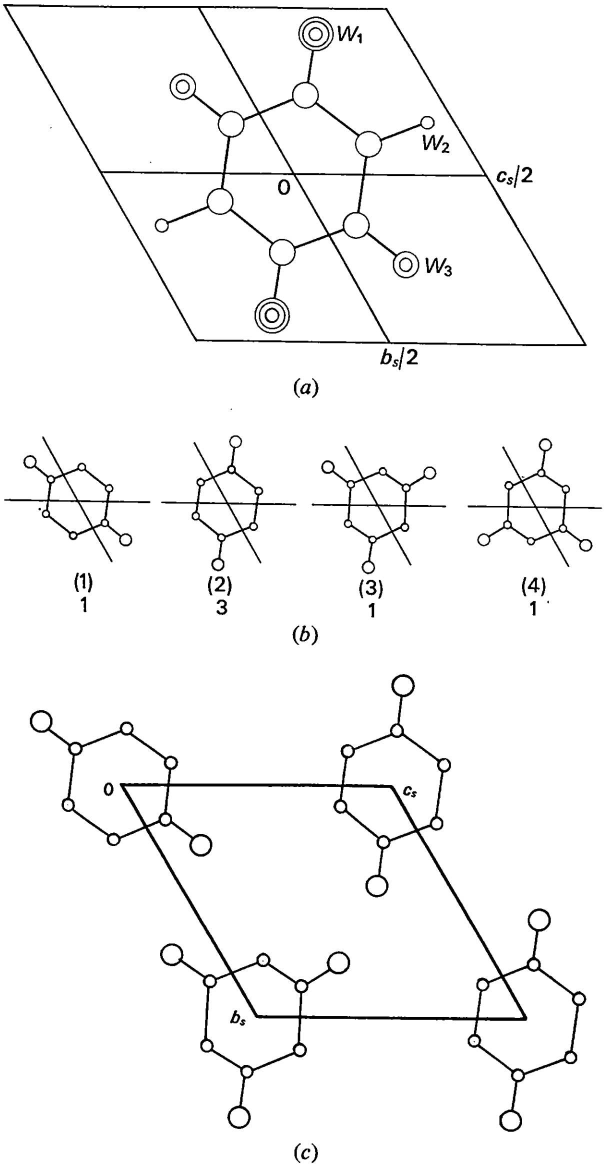


Fig. 2. (*a*) Hypothetical model for the subcell structure, (*b*) orientational types of molecules (numbers under the type numbers are those used in the unit cell), (*c*) a trial structure.

The shortest hydrogen bond 2·70 Å exists, between O(IV,2) and O(II,1). The angle C(II,1)–O(II,1)····· O(IV,2) is 172°, which is quite different from the ordinary value of about 120° for this type of compound. This result agrees well with the infrared spectrum of the O–H stretching vibration shown in Fig. 5, which indicates that one of the three hydrogen bonds has a different character from that of the other two.

The separation between the mean molecular planes $(\bar{3},\bar{1},1)$ is 3·18 Å. The reduction of the volume per formula unit compared with the sum of the component molecules is 4·0 %. This value is smaller than the value of about 8 % for the other quinhydrone-type complexes. This is naturally expected, because the number of acceptor molecules (quinone) is twice that of the donor molecules (phloroglucinol). The overlapping of molecular planes is shown in Fig. 6.

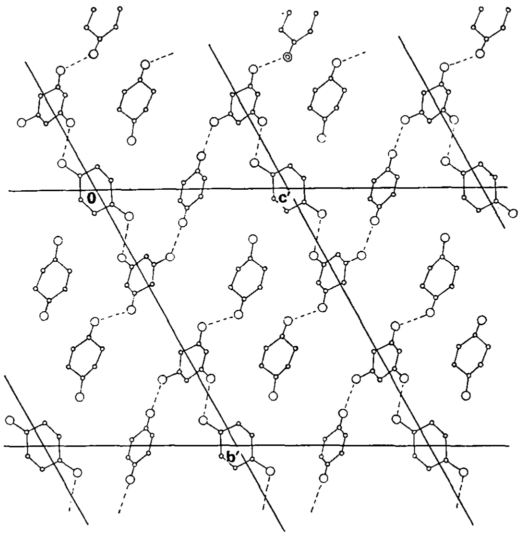
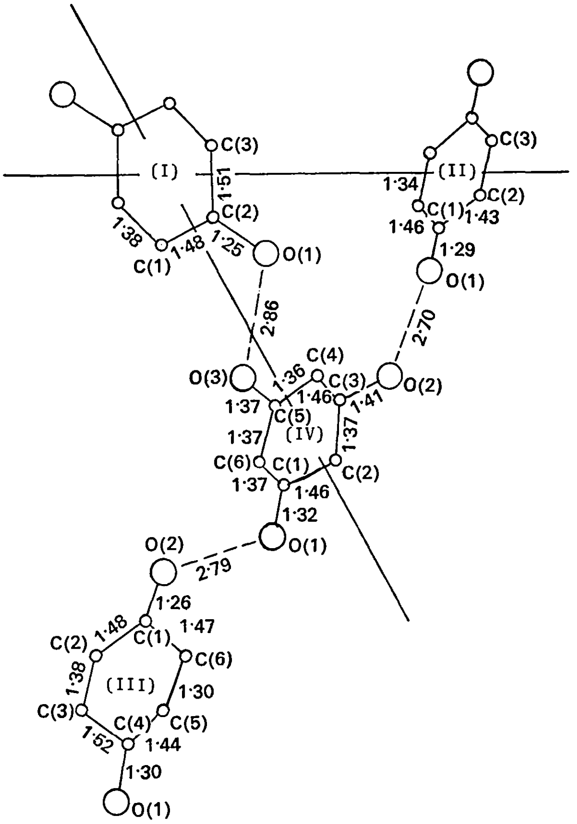


Fig. 3. Arrangement of the molecules on the **b**′ **c**′ plane.



(*a*)

Fig. 4. Structural unit: (*a*) bond distances. Molecules (I) and (II) have centers of symmetry. Mean standard deviations are 0·022 Å for C–C, 0·018 Å for C–O, 1·4° for C–C–C, 1·5° for C–C–O.

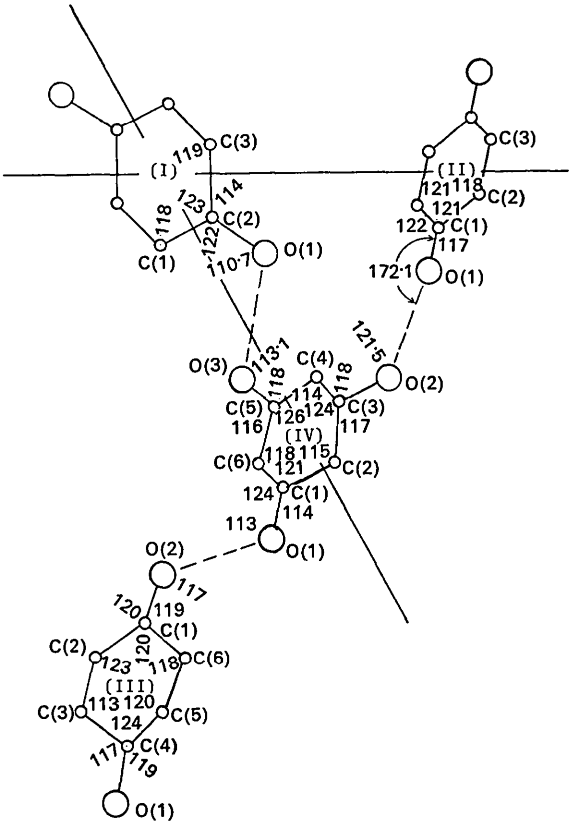


Fig. 4 (*cont*.) (*b*) bond angles.

The maximum overlapping occurs between molecules (IV) and (III), and some between (IV) and (II). It is interesting to see that, in spite of the over-population of the acceptor molecules on the molecular plane, their mutual overlapping is skilfully avoided. The intermolecular C–C distances shorter than 3·5 Å occur only between molecules (IV) and (III). In all other quinhydrone-type complexes, the shortest interatomic distance between the molecular layers, about 3·15 Å, occurs between the oxygen atom of the donor and the carbon atom of the acceptor molecule. A similar situation occurs in this case too. However, an interesting difference is that the shortest C···O distance, 3·12 Å, does not occur between overlapped molecules, but occurs between non-overlapped molecules (IV) and (I). These short interlayer distances are shown in Table 4.

Table 3. *Angles between the molecular planes*

	(II)	(III)	(IV)
(I)	7·9°	6·9°	9·2°
(II)		6·0	6·6
(III)			2·4

Table 4. *Short interlayer atomic distances*

(C···C; shorter than 3·5 Å,
C···O; shorter than 3·3 Å,
O···O; shorter than 3·3 Å.)

Corresponding distances are shown in Fig. 6.

C(IV, 2)····C(III, 5)	3·49 Å
C(IV, 4)····C(III, 1)	3·47
C(IV, 4)····C(III, 2)	3·28
C(IV, 5)····C(III, 2)	3·41
C(IV, 6)····C(III, 3)	3·42
C(I, 2)·····O(IV, 2)	3·26
C(I, 3)·····O(IV, 2)	3·12
C(III, 5)····O(IV, 1)	3·49
O(I, 1)·····O(IV, 2)	3·28

The best-fit planes through the molecules are as follows:

$$0{\cdot}9673x+0{\cdot}3297y-0{\cdot}4441z=\ 0 \qquad \text{(I)}$$
$$0{\cdot}9892x+0{\cdot}2809y-0{\cdot}3354z=0{\cdot}04843 \qquad \text{(II)}$$
$$0{\cdot}9687x+0{\cdot}2230y-0{\cdot}4206z=-1{\cdot}1402 \qquad \text{(III)}$$
$$0{\cdot}9678x+0{\cdot}1883y-0{\cdot}4047z=-0{\cdot}5958. \qquad \text{(IV)}$$

The mutual angles between these molecules are shown in Table 3.

The smallest angle of tilt, 2·4 is observed between molecules (III) and (IV) which exhibit the largest overllapping of the carbon rings, and the largest angle, 9·2° occurs between molecules (I) and (IV), which are related by the shortest C···O distance.

In this way, in spite of the complexity of the molecular arrangement, this complex exhibits, very clearly,

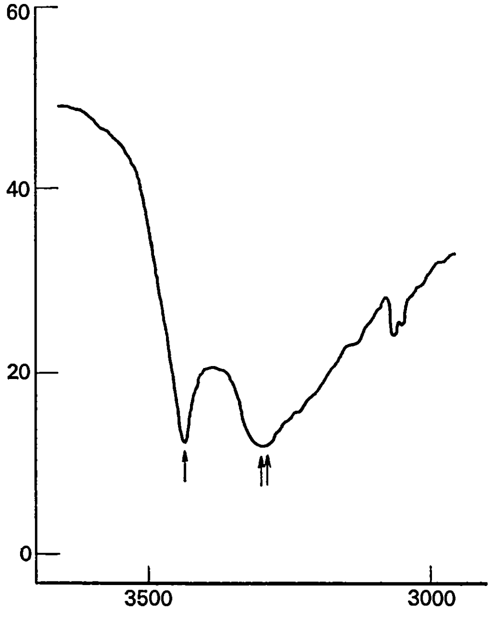


Fig. 5. Infrared spectrum. Arrows indicate the O–H stretching frequencies.

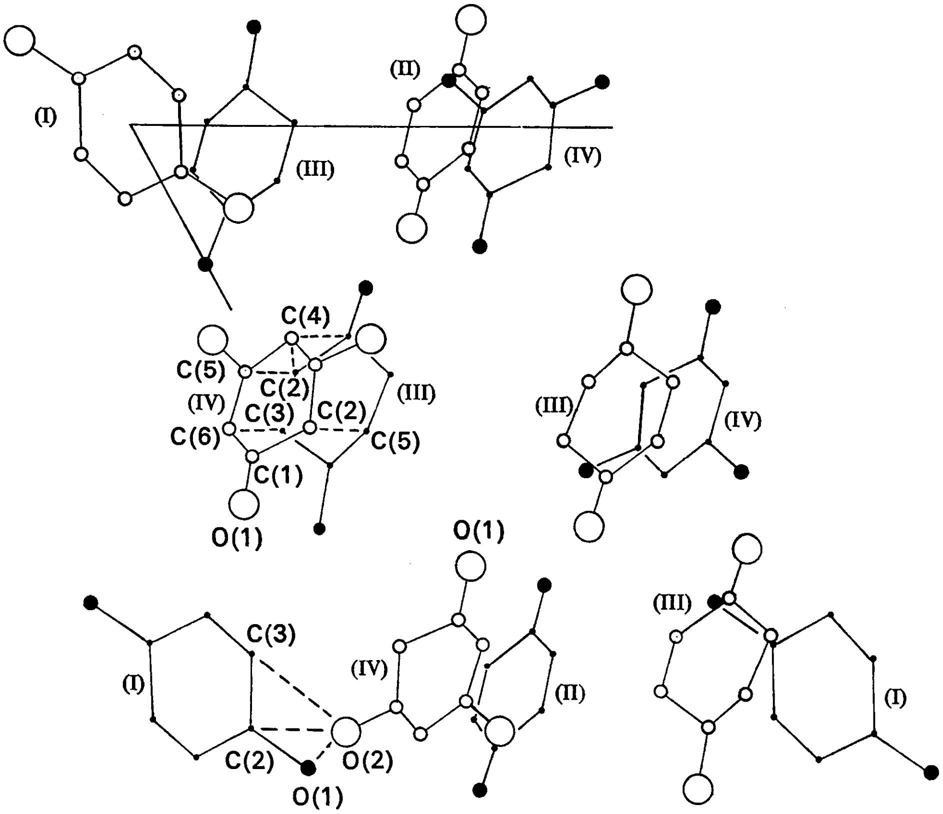


Fig. 6. Overlapping of the molecular planes. C···C distances shorter than 3.5 Å, and C···O distances shorter than 3.3 Å, are indicated in this figure by dashed lines.

the structural principle of quinhydrone-type complexes, that is, the formation of molecular chains by the hydrogen bond, parallel overlapping of the carbon rings of donor and acceptor, and the $C\cdots O$ attraction.

The numerical calculations were performed on the *FACOM* 270–30 computer of this Institute, and on the *HITAC* 5020E computer of the Computer Centre of the University of Tokyo, with a universal crystallographic computation program system, *UNICS* (Sakurai, 1967). The authors express their sincere thanks to Dr T. Ito for his assistance during the preliminary stage of data collection, and to Miss Kobayashi for her aid in the computation.

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The Crystal Structure of $POCl_3$

BY K. OLIE

Anorganisch Chemisch Laboratorium, Universiteit van Amsterdam, Nieuwe Achtergracht 123,
Amsterdam, the Netherlands

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The crystal structure of $POCl_3$ has been determined. Unit-cell dimensions are $a=9\cdot185\pm0\cdot003$, $b=9\cdot326\pm0\cdot002$, $c=5\cdot749\pm0\cdot001$ Å. The space group is $Pn2_1a$. Average P–Cl distance is 1·98 Å and the P–O distance is 1·46 Å. The molecules form infinite chains by means of an intermolecular Cl–O bond of length 3·05 Å.

Vibrational spectra of solid $POCl_3$ indicate intermolecular bonding (Smitskamp, Olie & Gerding, 1968; Olie & Mijlhoff, 1969) as for $POBr_3$. To obtain more information about this bonding we attempted the determination of the crystal structure.

Experimental

Cylindrically shaped single crystals of diameter 0·05 cm were grown in thin-walled glass capillaries by repeated melting and crystallization. Zero level Weissenberg photographs (Cu radiation) about [100] and [001] were superposed with Al powder lines for calibration. Carefully measured glancing angles corresponding to $0kl$ and $hk0$ reflexions were used to determine the unit-cell dimensions by a least-squares procedure (Table 1).

Table 1. *Crystal data of* $POCl_3$

Cell dimensions:	$a=9\cdot185\pm0\cdot003$ Å
	$b=9\cdot326\pm0\cdot002$
	$c=5\cdot749\pm0\cdot001$
Space group	$Pn2_1a$
Number of molecules per cell	$Z=4$
Calculated density	2·07 $g.cm^{-3}$
Absorption coefficient	$\mu=180\cdot4$ cm^{-1}

The listed errors correspond to three times the standard deviations. Systematically absent reflexions ($0kl$ for $h+k=2n+1$, $hk0$ for $h=2n+1$, $00l$ for $l=2n+1$) indicate as possible space groups: *Pnma* (No. 62) and $Pn2_1a$ (No. 33). The following non-integrated equi-inclination Weissenberg photographs (multiple-film technique) were made at about −100°C with Cu $K\alpha$ radiation: about [001] levels, $l=0$ to 4; about [100] levels, $h=0$, 1, 2. The reflexions were practically all slit-shaped; their intensities were scanned with a recording densitometer and the areas of the peaks were measured with a 'Kurvenauswerter' (a curve digitizing system, Atlas KA101). Thus it was not necessary to correct for α_1–α_2 splitting. The integrated intensities were corrected for absorption ($\mu R=4\cdot51$) and reduced to structure-factor moduli after accounting for Lorentz and polarization factors.

Several reflexions occurring on more than one film were used to put the structure factors on a common relative scale.

Structure determination and refinement

The cell dimensions of $POBr_3$ and $POCl_3$ are very similar, their axial ratios being nearly equal. A survey of the Patterson map showed that at least the chlorine atoms in $POCl_3$ are situated at nearly the same positions as the bromine atoms in $POBr_3$. We have chosen the space group $Pn2_1a$ (No. 33) as the basis of our re-