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The Crystal Structure of the 1:1 Molecular Complex of Thymine and *p*-Benzoquinone

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It was found that thymine $C_5H_6N_2O_2$, a component of the nucleic acid bases, forms a single-crystal of 1:1 molecular complex with *p*-benzoquinone $C_6H_4O_2$. The crystals are orthorhombic, space group *Pcmn*, with $a=12{\cdot}427$, $b=12{\cdot}639$ and $c=6{\cdot}859$ Å. The crystal consists of layer arrays of molecules. Thymine molecules are on the mirror planes at $y=\frac{1}{4}$ and $y=\frac{3}{4}$, and are connected by the hydrogen bond to form an infinite molecular ribbon. The quinone molecules are sandwiched between these planes and the molecular stacking is similar to that found in quinhydrone-type molecular complexes.

Introduction

Since the importance of DNA was recognized, a vast amount of work has been done to investigate the interactions of nucleic acid bases and other molecules. From X-ray diffraction (Lerman, 1961) and dichroism (Nagata, Kodama, Tagashira & Imamura, 1966) of DNA solutions, many molecules with potent mutagens or carcinogens, such as aromatic hydrocarbons, acridines and nitroquinoline derivatives are supposed to be intercalated between the planes of DNA bases. The crystals of the molecular complex between purine and the hydrocarbons were first obtained by Weil-Malherbe (1946), and the crystal structures of the 1:1 complex between 1,3,7,9-tetramethyluric acid(TMU) and pyrene (Damiani, De Santis, Giglio, Liquori, Puliti & Ripamonti, 1965), and the 2:1 complex between TMU and 3,4-benzpyrene (Damiani, Damiani, Giglio, Liquori & Ripamonti, 1967) were solved.

It was suggested by Szent-Györgyi (1960) that the weak charge-transfer force between donor and acceptor molecules might play an essential role in these interactions. The formation of the charge-transfer complex between nucleic acid bases and chloranil in dimethyl sulfoxide solution was reported by Machmer & Duchesne (1965). Single-crystals of the 1:1 complex of thymine and *p*-benzoquinone were obtained in our laboratory (Sakurai & Okunuki, 1969) and the structure was solved by X-ray diffraction (Sakurai, 1969).

Crystal data

Orthorhombic *Pcmn* (D_{2h}^{16})
$a=12{\cdot}427\pm0{\cdot}006$, $b=12{\cdot}639\pm0{\cdot}007$,
$c=6{\cdot}859\pm0{\cdot}003$ Å
$V=1077{\cdot}3\pm1{\cdot}0$ Å^3
Formula: $C_5H_6N_2O_2$:$C_6H_4O_2$ F.W.$=234{\cdot}2$
$D_m=1{\cdot}44$ g.cm^{-3}, $D_x=1{\cdot}444$ g.cm^{-3} with $Z=4$.

Experimental

Light-yellow prismatic crystals, elongated along the *c* axis were obtained from slow-cooling the dimethyl sulfoxide solution of the equal molar ratio of the component molecules. From the chemical analysis and density measurement, the formation of the 1:1 complex of the thymine and *p*-benzoquinone was ascertained. The crystals were sealed in thin-walled glass capillaries to avoid decomposition during the exposure. A total of 562 independent X-ray diffraction intensities were recorded with a single-crystal automatic diffractometer *RIKEN READ* 1 (Sakurai, Ito & Iimura, 1970) with monochromatized Mo $K\alpha$ radiation. These were corrected for the ordinary Lorentz and polarization factors, and were reduced to the absolute scale structure amplitude with the data-reduction program *RDTR*-3 (Sakurai, 1967).

Structure determination

The general positions are eightfold for this space group. Since the number of molecules in the unit cell is four, the molecules must be at some special positions. The point symmetries of special positions in this space group are $\bar{1}$ and *m*. The thymine molecule must be on a mirror plane, because it has no center of symmetry. The mirror planes in this space group are perpendicular to the *b* axis and are at $y=\frac{1}{4}$ and $\frac{3}{4}$. Therefore, it was assumed that the quinone molecules were around the centers of symmetry on the planes $y=0$ and $\frac{1}{2}$. In this special condition, the generalized Patterson function

$$P_1(x,z)=\int_0^1 P(x,y,z)\cos 2\pi y\,dy$$

$$=\frac{1}{ac}\sum_h\sum_l F^2(h1l)\exp[-2\pi i(hx+lz)]$$

consists of the interatomic vectors belonging to the thymine molecule alone. The length of the *c* axis, 6·86 Å, is almost equal to the distance between the neighbouring thymine molecules in the thymine monohydrate crystal (Gerdil, 1961). Therefore, the hydrogen-bond scheme was assumed to be the same as that found in the hydrate. Based on this assumption, and from the generalized Patterson function, a trial structure was easily deduced. The structure was refined by the ordinary full-matrix least-squares method with anisotropic temperature factors. From a difference Fourier synthesis computed at a later stage of the refinement (Fig. 1), all hydrogen-atom positions were obtained. These hydrogen parameters were included, but not refined in the final structure-factor calculation. F_o and F_c values are shown in Table 1. The R value for observed reflexions is 8·4 %. Atomic parameters are shown in Table 2.

Discussion of the structure

The crystal structure is shown in Fig. 2. It consists of layer arrays of molecules. The mirror planes perpendicular to the b axis pass through this axis at $y=\frac{1}{4}$ and $\frac{3}{4}$. Thymine molecules are on these planes and are connected by the hydrogen bond to form an infinite molecular ribbon along the c axis. The quinone molecules are sandwiched between thymine planes. The best-fit plane through the quinone molecule is

$$-0{\cdot}0193a+0{\cdot}9941b+0{\cdot}1067c=0.$$

This plane makes an angle of 6·2° with the (010) plane.

Intramolecular distances and angles as well as their thermal ellipsoids are shown in Fig. 3. There is no significant difference in the shape and size of quinone molecules with those reported previously (Trotter, 1960; Sakurai, 1968; Ito, Minobe & Sakurai, 1970).

The hydrogen-bonding scheme in thymine molecular ribbon is the same as that reported in thymine anhydrate (Ozeki, Sakabe & Tanaka, 1969) and its mono-

Table 1. *Observed and calculated structure factors*

K	FO	FC
0	K	0
2	38	-36
4	277	308
6	22	-22
8	122	117
10	14	-14
12	43	45
16	15	16
1	K	0
1	36	-33
3	43	40
5	23	-20
7	27	25
9	7	-8
11	9	9
2	K	0
0	101	101
2	28	28
4	75	72
6	4	5
8	36	33
12	15	14
16	6	5
3	K	0
1	17	15
3	11	-9
5	18	17
7	5	-5
9	7	8
11	5	-2
4	K	0
2	84	-81
4	39	-34
6	40	-38
8	15	-12
10	13	-13
5	K	0
1	36	35
3	41	-41
5	16	16
7	26	-28
9	7	7
11	12	-15
6	K	0
0	44	-44
2	27	-23
4	30	-32
6	5	-14
8	11	-14
10	6	-8
7	K	0
1	64	61
3	61	-60
5	33	35
7	29	-36
9	9	14
8	K	0
0	13	10
2	6	-6
4	9	8
6	5	-6
10	4	-4
9	K	0
1	5	0
10	K	0
2	6	-6
12	K	0
0	4	-6
2	6	-15
1	K	1
0	44	45
1	52	-51
2	48	48
3	70	70
4	33	31
5	10	-8
6	23	22
7	44	43
8	17	15
10	8	9
11	22	22
12	5	6
14	4	4
15	8	11
2	K	1
0	46	-45
1	13	13
2	33	-32
3	19	-18
4	36	-33
5	4	4
6	11	-10
7	13	-11
8	14	-13
11	4	-5
12	5	-4
13	2	0
3	K	1
0	23	23
1	19	15
2	18	-18
3	17	-14
4	16	16
5	6	3
6	11	-11
7	5	-4
8	5	6
10	5	-5
4	K	1
0	4	-4
1	22	22
2	16	14
3	19	-18
4	3	0
5	13	13
7	8	-8
9	5	4
5	K	1
0	14	-15
1	3	-4
2	15	-15
3	9	-8
4	13	-12
5	6	-7
6	12	-10
7	9	-10
8	7	-7
10	7	-6
11	5	-4
6	K	1
0	67	64
1	3	1
4	45	44
5	5	3
8	17	18
12	8	6
14	4	-3
7	K	1
0	24	-24
1	7	-7
3	7	5
4	18	-18
5	8	-9
7	4	2
8	8	-9
9	7	-7
8	K	1
1	8	10
2	10	9
3	8	-9
5	5	7
6	5	5
9	K	1
1	4	4
3	5	-6
7	6	-6
10	K	1
10	5	0
11	K	1
0	10	-10
1	16	-17
2	11	14
3	11	12
4	9	-9
5	16	-16
6	7	9
7	5	6
9	9	-10
0	K	2
0	37	-41
1	30	32
2	41	-43
3	23	-24
4	22	-21
5	19	19
6	21	-23
7	7	-7
8	5	-3
9	10	10
10	5	-6
1	K	2
0	24	23
1	4	3
2	26	24
3	13	-13
4	16	15
6	10	10
7	11	-13
8	4	5
10	6	2
2	K	2
0	31	30
1	30	-31
2	74	-74
3	31	32
4	21	19
5	13	-13
6	38	-36
7	19	19
8	9	8
9	3	-2
10	15	-14
11	9	10
14	4	-5
15	4	5
3	K	2
0	18	-18
1	15	-14
2	54	47
3	9	9
4	16	-15
5	13	-14
6	28	25
8	10	-9
9	6	-6
10	10	10
12	4	-4
4	K	2
0	2	-2
1	15	15
3	3	-6
4	12	-2
5	13	14
6	3	-3
9	4	6
10	6	-5
5	K	2
0	16	-17
1	23	24
2	17	-16
3	12	-13
4	13	-13
5	21	22
6	7	-7
7	3	-2
8	7	-7
9	11	11
12	3	-3
6	K	2
0	5	5
1	5	-5
4	3	4
5	5	-6
9	4	-5
7	K	2
0	14	-12
1	9	10
3	3	-4
4	9	-8
5	12	12
6	3	-2
9	8	9
13	4	5
8	K	2
0	15	14
1	17	-17
3	10	9
4	13	13
5	19	-19
7	3	2
8	10	10
9	13	-14
12	7	6
13	7	-8
9	K	2
0	25	25
1	15	14
10	K	2
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2	7	10
3	14	15
4	19	19
5	16	-16
9	K	2
3	14	-14
4	21	20
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7	9	-8
8	11	11
9	5	5
12	4	5
10	K	2
7	8	9
8	12	12
9	11	-11
11	4	4
12	5	6
11	K	2
0	6	8
1	6	-6
2	15	16
4	6	6
5	5	-5
6	10	10
8	4	4
10	5	5
12	K	2
0	4	-3
2	8	9
4	4	-3
6	5	6
13	K	2
2	5	-5
1	K	3
0	8	-7
2	5	6
4	8	-6
8	7	-6
2	K	3
0	5	2
1	44	40
2	36	34
3	31	-28
5	33	30
6	19	17
7	14	-12
9	14	14
3	K	3
0	56	-53
2	31	-29
3	3	2
4	41	-39
6	15	-15
8	18	-19
4	K	3
0	19	-18
1	27	24
2	4	3
3	25	-21
4	15	-15
5	19	17
6	4	4
7	14	-14
8	6	-8
9	9	10
5	K	3
0	11	-9
2	25	-24
4	8	-7
6	13	-13
8	6	-3
11	4	1
6	K	3
0	23	-23
1	6	8
2	11	-10
3	10	-10
4	17	-16
6	7	-7
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8	7	-7
7	K	3
0	16	15
1	7	-7
2	36	35
3	5	4
4	12	11
5	5	-5
6	25	24
8	5	4
10	10	12
8	K	3
1	17	-18
2	8	-9
3	18	19
4	4	3
5	12	-12
6	6	-6
7	14	14
9	K	3
0	13	-16
1	16	-17
2	64	67
3	16	17
4	14	-14
5	12	-13
6	45	47
7	12	12
8	9	-10
9	6	-7
10	21	26
10	K	3
2	4	6
4	4	4
5	4	5
6	5	3
11	K	3
0	5	-7
1	4	-5
0	K	4
0	10	13
1	11	-11
2	3	0
3	12	12
4	7	8
5	8	-6
9	5	-5
13	4	-4
1	K	4
0	14	-14
4	10	-10
6	3	3
8	3	-3
2	K	4
1	28	27
2	12	-9
3	30	-28
5	15	15
6	6	-6
7	20	-19
9	4	4
11	9	-10
3	K	4
0	12	13
2	22	-22
3	5	-5
4	12	11
6	12	-11
7	6	-5
8	8	8
4	K	4
0	6	-6
1	7	-9
2	8	-8
4	5	-5
5	8	-10
6	4	-5
7	7	-5
9	7	-6
5	K	4
0	4	-3
1	6	6
2	13	16
3	6	-7
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6	K	4
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6	5	4
7	K	4
0	6	-6
4	7	-7
8	K	4
0	5	4
1	8	8
2	12	11
5	11	12
6	9	8
9	10	10
9	K	4
0	27	-28
2	4	2
4	22	-23
8	12	-13
10	K	4
1	10	10
2	5	5
3	6	-7
5	9	11
6	5	4
9	9	8
11	K	4
0	4	2
2	7	-7
12	K	4
0	6	-9
1	7	-7
3	6	6
4	6	-7
5	6	-6
7	4	4
8	4	-5
13	K	4
2	4	5
1	K	5
0	7	-8
1	16	15
2	23	22
3	17	-18
4	6	-6
5	8	9
6	19	18
7	14	-14
8	3	-2
10	10	12
11	9	-9
2	K	5
0	11	13
1	5	4
2	17	18
3	8	-9
4	10	10
6	11	12
7	9	-8
8	7	6
10	4	5
11	4	-5
3	K	5
0	16	15
2	9	10
4	12	11
6	4	6
8	5	5
4	K	5
1	6	4
2	13	13
3	3	-5
6	9	9
7	6	-2
10	5	5
5	K	5
2	3	2
8	3	-2
6	K	5
0	18	-18
1	7	-7
3	8	9
4	15	-15
5	5	-4
6	4	4
7	6	6
8	9	-9
10	3	2
7	K	5
0	19	-20
4	16	-16
8	9	-9
8	K	5
0	10	-12
2	4	-4
3	3	-2
4	9	-10
6	3	-3
7	3	-2
8	4	-6
9	K	5
0	8	-8
1	5	-6
2	5	-5
3	6	6
4	7	-7
6	3	-3
7	4	4
8	4	-4
10	K	5
5	4	-4
9	4	-3
11	K	5
0	14	-15
2	11	12
4	13	-13
6	7	8
12	K	5
0	5	5
5	4	3
0	K	6
0	52	53
1	34	33
2	11	-11
3	29	-31
4	43	45
5	25	25
6	7	-9
7	19	-20
8	26	27
9	15	16
10	6	-6
11	9	-10
12	11	13
1	K	6
0	17	17
1	9	-9
3	7	9
4	13	14
5	5	-5
7	5	6
8	7	8
9	3	-3
10	2	0
2	K	6
0	14	12
1	9	9
2	6	6
3	7	-7
4	11	10
5	9	9
6	3	4
7	5	-5
8	7	7
9	7	7
11	3	-2
3	K	6
0	8	8
2	15	16
4	5	6
6	9	11
8	3	3
10	4	5
4	K	6
0	7	-8
1	5	5
2	5	-5
4	4	-6
5	5	6
6	3	-3
8	3	-3
9	3	4
5	K	6
0	9	-10
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4	7	-9
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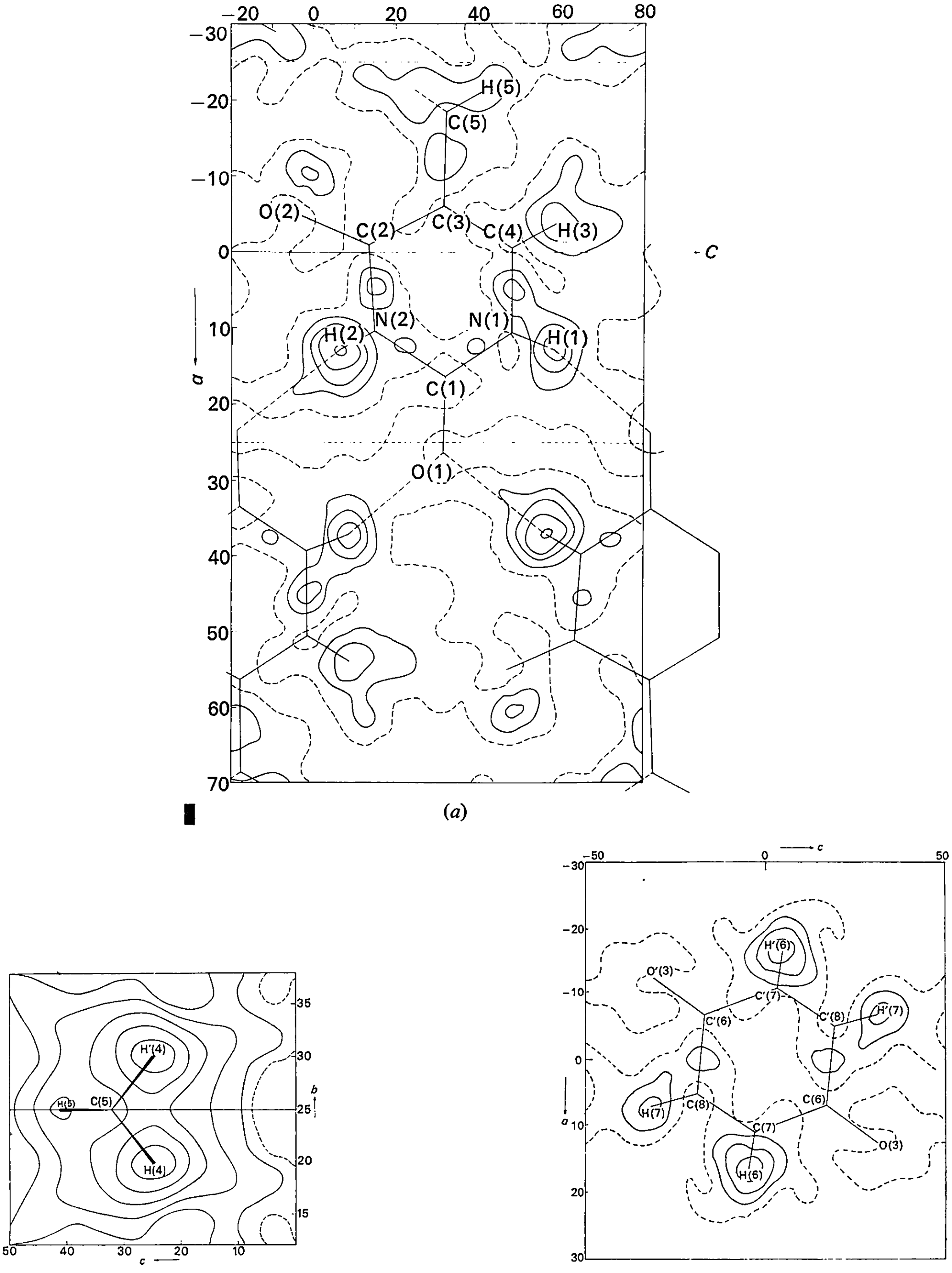
7	5	-5
8	6	-5
9	3	3
6	K	6
4	7	-8
8	5	-4
7	K	6
2	6	10
3	11	-14
4	14	-16
5	7	9
6	7	8
7	9	-10
8	8	-10
9	4	4
8	K	6
2	3	-5
3	4	-3
9	K	6
0	4	-1
2	3	6
4	4	-1
10	K	6
2	3	-3
11	K	6
2	3	2
4	3	2
1	K	7
0	7	6
3	8	9
4	6	5
2	K	7
0	6	-6
3	K	7
1	6	8
3	7	-7
5	8	7

hydrate (Gerdil, 1961). The intramolecular bond distances for these three structures are compared in Table 3. The standard deviations for bond lengths are, though different from structure to structure, about 0·015 to 0·02 Å. Within these standard deviations, the three structures agree well, except for the length of C(2)–C(3). The bond orders p corresponding to the mean bond lengths r are calculated by Coulson's (1939) for-



(a)

(b)

(c)

Fig. 1. Difference Fourier synthesis. Contours are at intervals of 0·2 e.Å^{-3} for (a) and (c), and of 0·1 e.Å^{-3} for (b). (a) A section through the thymine molecular plane, (b) a section through the methyl hydrogen plane, (c) a section through the quinone molecular plane.

mula,

$$r = r_s - \frac{r_s - r_d}{1 + K(1-p)/p},$$

where r_s and r_d are single- and double-bond lengths respectively. K is a constant and the following values were used: 0·765 for the C–C bond and 0·6625 for the

Table 2. *Atomic parameters*

Atomic coordinates with standard deviations (× 10^4)

Thymine	x/a	y/b	z/c
O(1)	2640 (6)	2500	3135 (13)
O(2)	−481 (6)	2500	−294 (11)
N(1)	1057 (7)	2500	4810 (14)
N(2)	1042 (9)	2500	1484 (16)
C(1)	1651 (12)	2500	3184 (20)
C(2)	−97 (9)	2500	1331 (17)
C(3)	−607 (10)	2500	3150 (20)
C(4)	−67 (11)	2500	4820 (20)
C(5)	−1847 (13)	2500	3219 (21)
H(1)	1280	2500	6100
H(2)	1400	2500	250
H(3)	−450	2500	6010
H(4)	−2100	1900	2500
H(5)	−2200	2500	4410

Quinone	x/a	y/b	z/c
O(3)	1257 (6)	−145 (6)	3091 (9)
C(6)	686 (8)	−96 (8)	1668 (13)
C(7)	1103 (7)	29 (10)	−297 (15)
C(8)	501 (8)	128 (7)	−1889 (13)
H(6)	1860	76	−452
H(7)	702	200	−3200

Temperature factors (× 10^4)

Thymine	B_{11}	B_{22}	B_{33}	B_{12}	B_{23}	B_{31}
O(1)	16 (7)	99 (8)	144 (19)	0	0	−10 (9)
O(2)	17 (11)	69 (7)	140 (19)	0	0	−9 (9)
N(1)	29 (8)	80 (9)	72 (24)	0	0	4 (9)
N(2)	27 (8)	61 (8)	112 (29)	0	0	13 (10)
C(1)	65 (11)	44 (9)	97 (27)	0	0	−14 (14)
C(2)	26 (8)	46 (9)	104 (33)	0	0	−7 (11)
C(3)	32 (10)	57 (10)	141 (31)	0	0	6 (15)
C(4)	40 (10)	59 (10)	154 (28)	0	0	30 (11)
C(5)	62 (14)	126 (16)	154 (28)	0	0	−2 (15)
Quinone						
O(3)	77 (6)	105 (7)	232 (17)	3 (5)	5 (11)	−36 (9)
C(6)	46 (7)	58 (7)	201 (25)	−1 (6)	4 (12)	−26 (9)
C(7)	36 (8)	63 (7)	233 (24)	−5 (7)	−1 (11)	11 (10)
C(8)	57 (7)	53 (7)	185 (20)	6 (6)	6 (11)	−4 (11)

Expression of the temperature factor:

$$\exp\left[-(B_{11}h^2 + B_{22}k^2 + B_{33}l^2 + 2B_{12}hk + 2B_{23}kl + 2B_{31}lh)\right].$$

The B_{12} and B_{23} of the thymine molecule are zero, because the molecule is on the mirror plane perpendicular to the b axis.

Table 3. *Bond lengths and bond orders* (p) *of the thymine molecule*

	Bond length (Å)				Bond order	
	Thymine in the complex (present)	Thymine (Ozeki *et al.*, 1969)	Thymine monohydrate (Gerdil 1961)	Mean length	Calculated from the mean length	Theoretical for uracil (Miyata *et al.*, 1966)
O(1)–C(1)	1·229	1·246	1·234	1·236		0·79
O(2)–C(2)	1·212	1·193	1·231	1·212		0·79
N(1)–C(1)	1·337	1·314	1·355	1·335	0·63	0·54
N(1)–C(4)	1·398	1·408	1·382	1·396	0·31	0·30
N(2)–C(1)	1·390	1·345	1·361	1·365	0·46	0·34
N(2)–C(2)	1·419	1·413	1·391	1·408	0·26	0·32
C(2)–C(3)	1·400	1·476	1·447	1·441	0·39	0·36
C(3)–C(4)	1·327	1·369	1·349	1·348	0·94	0·89
C(3)–C(5)	1·542	1·522	1·503	1·522	0·08	

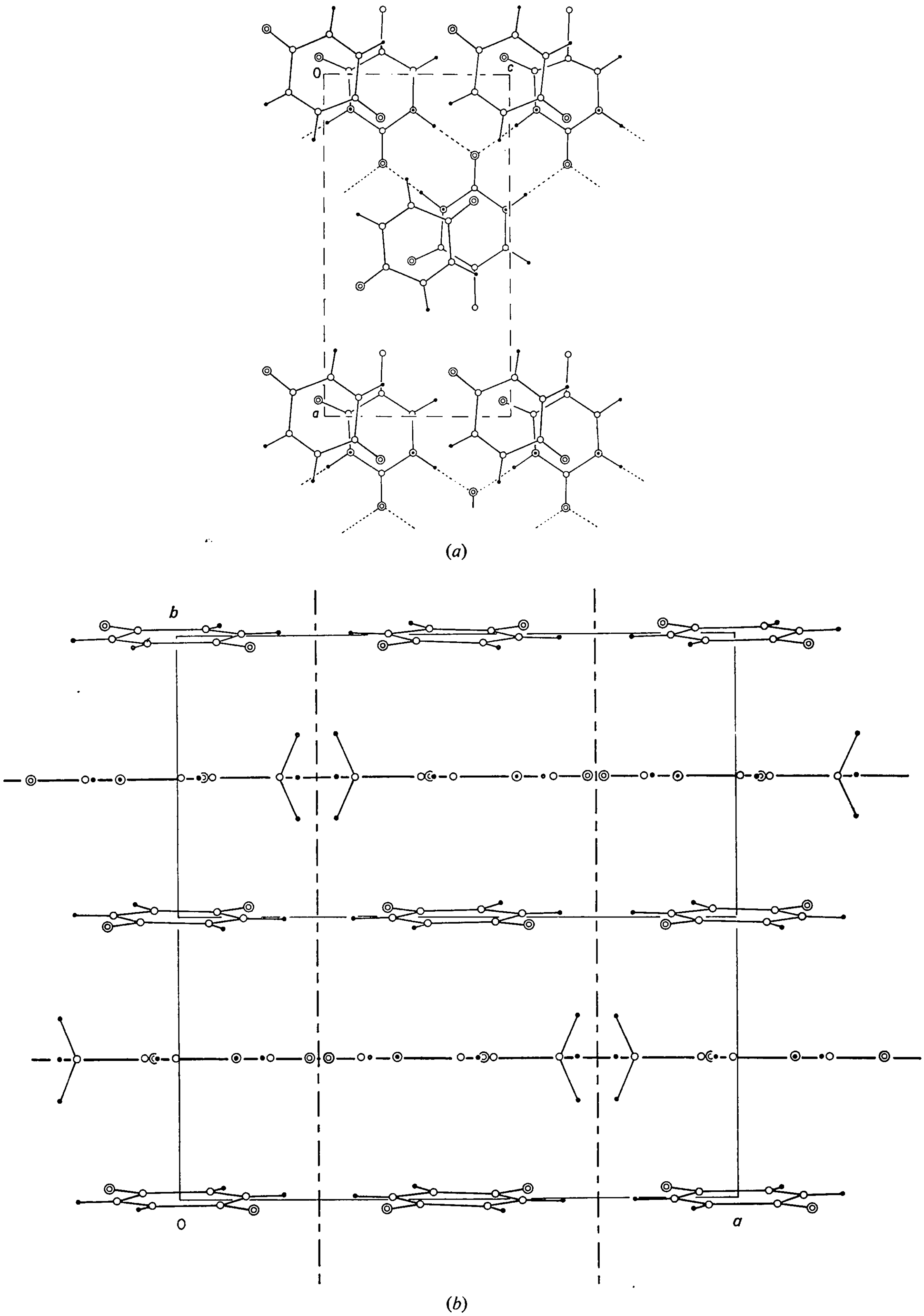


Fig. 2. The crystal structure, (*a*) viewed along the *b* axis, (*b*) viewed along the *c* axis. ◎: Oxygen atom, ⊙: Nitrogen atom, ○: Carbon atom, ●: Hydrogen atom.

C–N bond (Liquori & Vaciago, 1965). These are also shown in Table 3.

From the mean bond distances, it is clearly shown that C(1)–N(1) is shorter than other C–N distances and C(2)–C(3) is longer than C(3)–C(4). Ozeki *et al.* (1969) discussed the resonance contribution of the enol form (Fig. 4), in order to explain the short C(1)–N(1) and C(1)–N(2) distances. However, the present result shows that both H(1) and H(2) appear equally well on the difference map [Fig. 1(*a*),] and the C(1)–O(1) length equals the ordinary double-bond length within experimental error. On the other hand, the values of bond order agree, at least qualitatively, with the theoretical values (the last column of Table 3) for the normal state of uracil (Miyata, Suzuki & Yomosa, 1968).Although there is no theoretical value for the bond order that can be directly compared with the observed one, the π-bond structure is not much different for thymine and

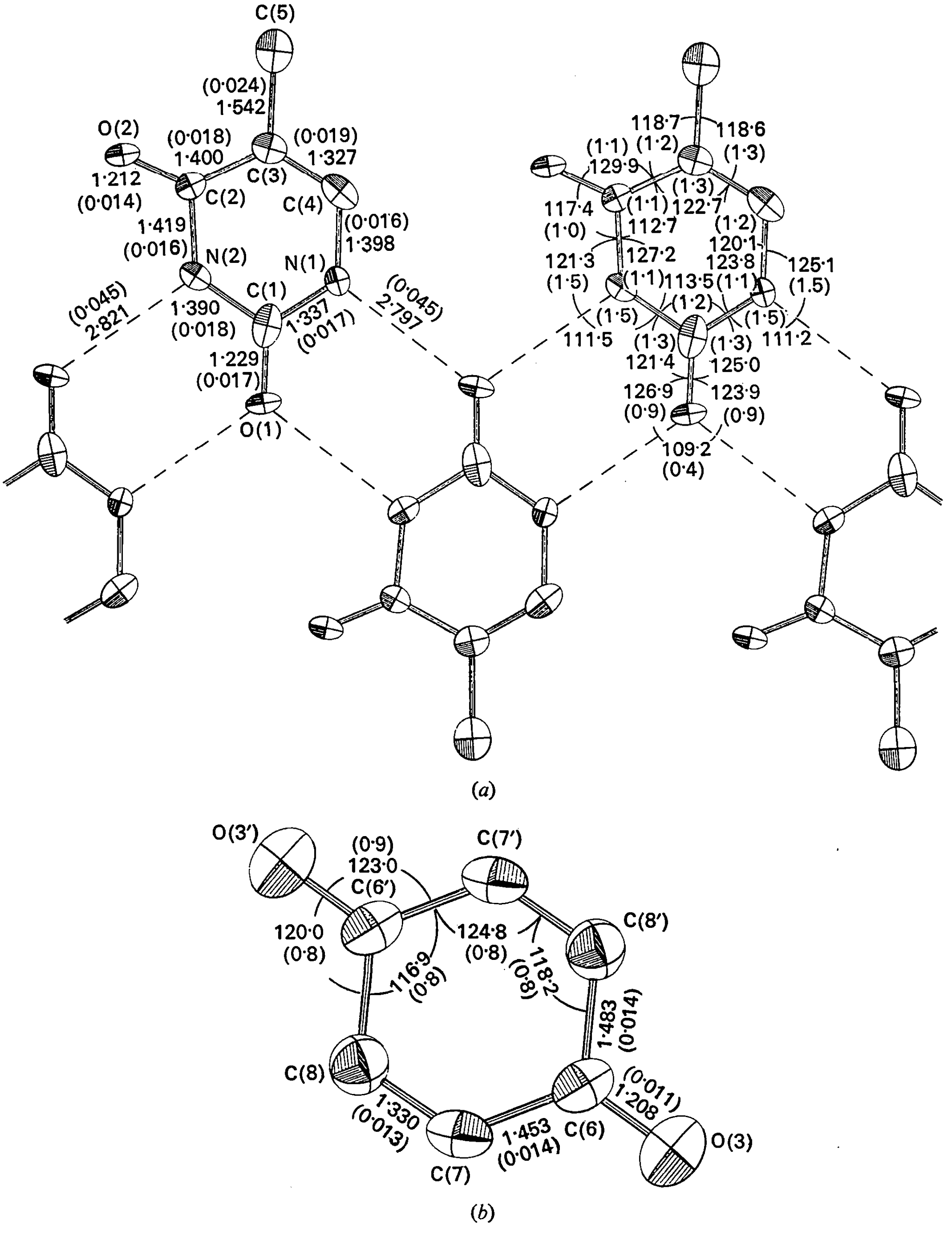


Fig. 3. Bond angles and distances. Thermal ellipsoids as viewed along the *b* axis. Standard deviations are in parentheses. (*a*) Thymine molecular ribbon, (*b*) quinone molecule.

uracil.* Therefore, these bond-length differences are not attributed to the resonance structure.

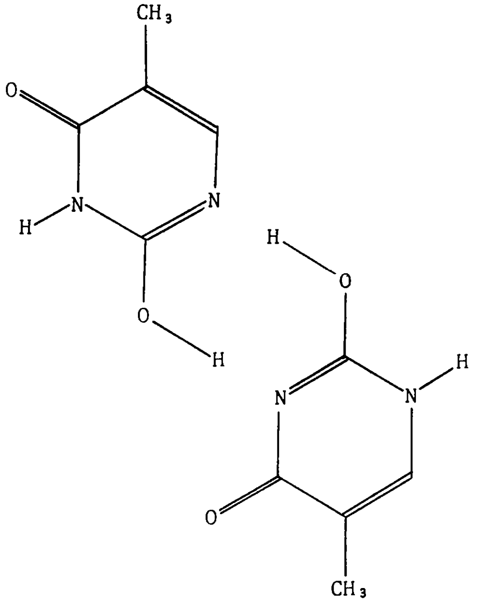


Fig. 4. Enol form of thymine molecule.

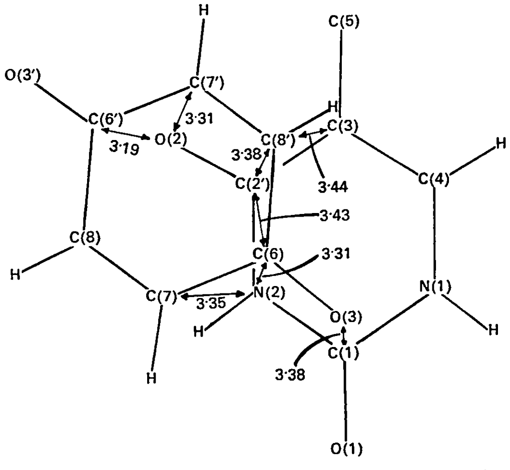


Fig. 5. Interatomic distances between molecular planes.

The stacking of the molecular planes is shown in Fig. 5. In contrast with the thymine monohydrate and anhydrate, where the overlapping of the molecules betwen neighbouring layers is slight, parts of the molecular rings are overlapped. The shortest intermolecular atomic distance is 3·19 Å between the oxygen atom in the thymine molecule and the C(6) atom in the quinone molecular ring. This distance is considerably shorter than that found in the mutual disposition of the many pyrimidine bases as shown in Fig. 6, and is similar in length to that found in the quinhydrone type molecular complexes (Sakurai, 1965, Sakurai, 1968; Ito, Minobe & Sakurai, 1970). Therefore, the short oxygen–carbon interaction may be important in determining the mutual disposition of molecules. This is also supported by the fact that the quinone molecular plane is inclined at an angle of 6·2° to that of the thymine molecules, as if they are attracted by the carbon–oxygen interaction mentioned above. The situation is very similar to that found in the quinone:resorcinol complex (Ito, Minobe & Sakurai, 1970).

The anisotropic temperature factors of atoms were transformed into a rigid-body vibration of the molecule. The results are shown in Table 4. The quinone molecule is subjected to larger thermal vibrations than those found in quinhydrone-type crystals. This is due to the different environment of the quinone molecule. In the quinhydrone-type structures, the quinone molecule is connected to the neighbouring hydroquinone molecules by the hydrogen bonds, whereas in the present structure, no such connection exists. For the thymine molecule, the root-mean-square displacement of atoms perpendicular to the molecular plane is considerably larger than that in the plane. It is naturally expected that the molecular motion in the plane is restricted by the hydrogen bond. Therefore, the rigid-body libration is subjected to the large anisotropy shown in Table 4.

At about 70 °C, the quinone molecules escape rapidly from the complex, leaving a white thymine crystal. The X-ray diffraction pattern of the thymine crystal, after decomposition of the complex, shows that the remaining thymine has a twin-like structure whose a_t and c_t axes coincide with those of the original (a and b axes of the complex, respectively). Thymine crystal belongs to the monoclinic system with $a_t = 12{\cdot}87$, $b_t = 6{\cdot}83$, $c_t = 6{\cdot}70$ Å and $\beta_t = 105°$. Since the dimension of the ac plane of the complex is similar to the dimension of the

Table 4. *Tensors of rigid-body vibration of the molecules*

The tensors refer to the principal axes of the moment of inertia of the molecules. The order of the axes corresponds to the increasing order of the principal values.

	Translational		Rotational	
Thymine	$\begin{pmatrix} 25 & -1 & 0 \\ -1 & 27 & 0 \\ 0 & 0 & 32 \end{pmatrix}$	10^{-3} Å^2	$\begin{pmatrix} 30 & -8 & 0 \\ -8 & 19 & 0 \\ 0 & 0 & 3 \end{pmatrix}$	deg.^{2}
Quinone	$\begin{pmatrix} 38 & 6 & 0 \\ 6 & 38 & 2 \\ 0 & 2 & 32 \end{pmatrix}$	10^{-3} Å^2	$\begin{pmatrix} 25 & 10 & -5 \\ 10 & 25 & 2 \\ -5 & 2 & 17 \end{pmatrix}$	deg.^{2}

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* The differences between the bond orders of thymine and uracil are about 0·01 or less (Yomosa, 1970).

a_tb_t plane of thymine, it is conceivable that the thymine plane is not affected too much by the decomposition. The relation between the crystal axis of thymine and that of the complex is shown in Fig. 7. The layer separation in the complex, $b/4 = 3{\cdot}16$ Å, is significantly smaller than the corresponding separation ($c_t \sin \beta_t/2 = 3{\cdot}24$ Å), in the thymine crystal.

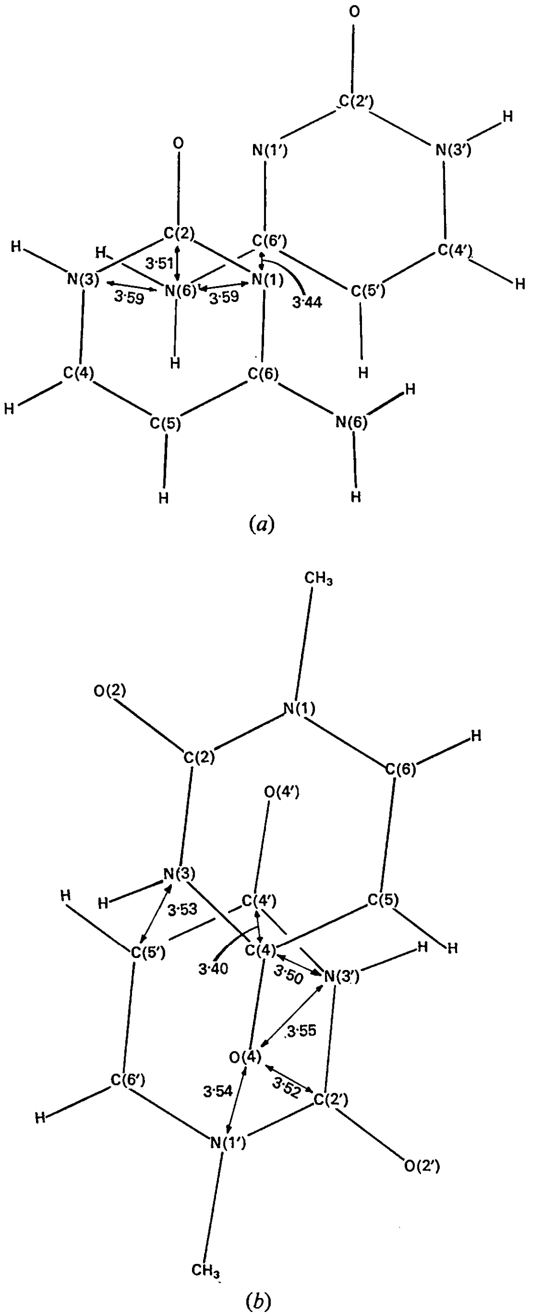

Fig. 6. Interatomic distances between molecular planes of related pyrimidine bases. (*a*) cytosine monohydrate (Jeffrey & Kinoshita, 1963), (*b*) *N*-methyluracil (Mathews & Rich, 1964).

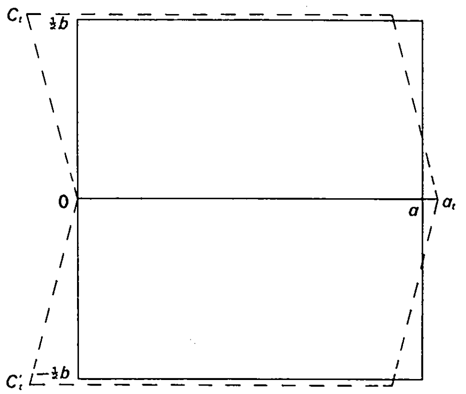

Fig. 7. The relation between the crystal axis of the complex crystal and that of twinned thymine crystal.

Although no spectroscopic observation has been done yet, it can be concluded, from the evidence described above, that the quinone molecules are trapped as guest molecules in the thymine skeleton by the weak charge-transfer force. We have made various attempts to grow the complex crystals of other combinations of nucleic acid bases and acceptor molecules. Many combinations show the clear change of color in solution. However, few of them were obtained as single crystals suitable for X-ray study. This means that the condition of the crystal formation depends not only on the charge transfer interaction, but also on some geometrical factors. The success of growing single crystals of the present complex stems from the volume similarity of these two kinds of molecules. The mean volume of the thymine in the anhydrous crystal is $142{\cdot}6$ Å^{-3}, whereas that of the quinone is $135{\cdot}5$ Å^{-3} (Trotter, 1960). The volume per complex is $269{\cdot}2$ Å^{-3}. This means that the formation of the complex comes a 3% contraction of the volume.

The main part of the numerical calculations was performed on the *FACOM* 270-30 computer of this Institute, using the universal crystallographic computation program system *UNICS* (Sakurai 1967). Fig. 3 is drawn with a plotter using *ORTEP* (Johnson, 1965).

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

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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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