α-$Zr(SO_4)_2$ gives rise to a planar network in which each zirconium atom is situated at the intersection of three chains of dimeric rings (Fig. 3), similar to the network found in a layer of γ-monohydrate (Bear & Mumme, (1970*a*). Thus the structure of α-$Zr(SO_4)_2$ may be visualized as being built up from layers of α-monohydrate, lying normal to the [010] direction in α-$Zr(SO_4)_2$, which are cross-linked in the [010] direction so that the chains of dimeric rings in the layers of monohydrate are joined to form the planar network of rings in the anhydrate structure. Alternatively the α-$Zr(SO_4)_2$ structure may be viewed as being derived from layers of the γ-monohydrate, lying normal to the [001] direction in α-$Zr(SO_4)_2$, which are cross-linked in the [001] direction to give the three dimensional network of the anhydrate structure.

It can be seen therefore, that although the structure of α-$Zr(SO_4)_2$ can be described as being made up of sheets of dimeric rings held together by Zr–O–S cross-linkages, it is in effect an intermeshing of the two distinct forms of layers found in the γ and α-monohydrates. In the removal of the water molecules from either one of these two monohydrates and the subsequent linking up of the layers, the anhydrate retains in its structure the characteristic form of the layers already present in the parent monohydrate and gains through the cross-linking the characteristic form of the layers of the other monohydrate. This effect is shown diagrammatically in Fig. 4 and supports the argument put forward above that both these transformations proceed with little breaking of the bonds within the layers of the parent compound.

Throughout this investigation we were fortunate to have the support and guidance of the late Dr A. D. Wadsley. His great enthusiasm for all aspects of the solid state was a continuing source of encouragement to us.

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The Crystal Structure of Quinone–Resorcinol Molecular Complex

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The crystal structure of *p*-benzoquinone–resorcinol molecular complex $C_6H_4O_2.C_6H_4(OH)_2$ has been determined from three-dimensional X-ray diffraction data. The crystal is orthorhombic, space group *Pnca*, with $a=14{\cdot}653$, $b=5{\cdot}976$, $c=11{\cdot}529$ Å, $Z=4$. Quinone and resorcinol molecules are alternatively linked side by side by hydrogen bonds ($O\cdots O=2{\cdot}747$ Å) to form infinite molecular chains. These chains are packed plane-to-plane by the charge transfer force to form a molecular sheet. The molecular planes of quinone and resorcinol in a sheet are almost parallel, the perpendicular distance between the molecular planes being about 3·1 Å. Overlap of the six-membered carbon rings of quinone and resorcinol is very small. This pattern of molecular arrangement is very similar to those of quinhydrones reported thus far.

Introduction

This is the third report of a series of crystal structure analyses of the charge transfer complexes between *p*-benzoquinone (electron acceptor) and hydroxybenzenes (electron donors); the structure of triclinic quinhydrone (β-form) and the refinement of the structures of phenoquinone and monoclinic quinhydrone (α-form) have already been reported (Sakurai, 1965, 1968).

Hydroquinone, the donor component of quinhydrones, is a *para* isomer, whereas resorcinol is a *meta* isomer, of dihydroxybenzenes. It will be interesting to see the effect of this isomerism on the molecular arrangements in these complexes. Preparation of crystals of quinone–resorcinol complex was reported by Michaelis & Granick (1944). Charge transfer absorption bands of this complex were observed by Amano (1969).

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Crystal data

p-Benzoquinone–resorcinol,
$C_6H_4O_2.C_6H_4(OH)_2$; F.W. 218·21
Orthorhombic prismatic along the *a* or *b* axes,
$a = 14{\cdot}653$ (0·005),* $b = 5{\cdot}976$ (0·002),
$c = 11{\cdot}529$ (0·003) Å,
$V = 1009{\cdot}6$ (0·6) Å^3.
$D_m = 1{\cdot}43$ g.cm^{-3} by flotation, $Z = 4$,
$D_x = 1{\cdot}44$ g.cm^{-3}.
Space group *Pnca* from systematic absences.

Table 1. *Atomic coordinates with standard deviations* ($\times 10^4$)

The coordinates without standard deviations are special positions.

Quinone	x/a	y/b	z/c
O(1)	704 (3)	−3494 (7)	1108 (4)
C(1)	390 (4)	−1871 (10)	584 (5)
C(2)	−87 (4)	−88 (11)	1237 (5)
C(3)	−466 (4)	1668 (10)	677 (5)
H(1)	−100 (60)	−140 (170)	2210 (80)
H(2)	−940 (50)	2750 (140)	1180 (70)
Resorcinol			
O(2)	1596 (3)	3260 (7)	−147 (4)
C(4)	2500	0	2299 (8)
C(5)	2046 (4)	1721 (12)	1711 (6)
C(6)	2039 (4)	1685 (10)	516 (5)
C(7)	2500	0	−121 (8)
H(3)	2500	0	3280 (110)
H(4)	1580 (50)	2610 (150)	2110 (70)
H(5)	1290 (60)	4280 (140)	270 (70)
H(6)	2500	0	−980 (100)

* Throughout this paper, the figures in parentheses are the estimated standard deviations.

Experimental

Deep-red crystals of quinone–resorcinol molecular complex were obtained from equi-molar ether solutions of *p*-benzoquinone and resorcinol. Prisms elongated along the *a* axis were obtained by slow evaporation (for a few days) of a dilute solution, whereas those elongated along the *b* axis were obtained by rapid evaporation (for a few hours) of a saturated solution, both at room temperature. The unit-cell dimensions were determined from twenty high-angle reflexions on rotation photographs recorded by Straumanis' method around the *a* and *b* axes. The wavelengths used were 1·54051 and 1·54433 Å for Cu $K\alpha_1$ and α_2 radiations respectively.

Sets of multiple-film Weissenberg photographs were obtained by the use of an integrating cassette up to the 13th layer around the *a* axis, and up to the 5th layer around the *b* axis with Ni-filtered Cu $K\alpha$ radiation. The cross sections of the crystals used for the intensity measurements were about $0{\cdot}30 \times 0{\cdot}35$ and $0{\cdot}15 \times 0{\cdot}25$ mm for the *a* and *b* axes respectively. Since the crystals gradually decompose on exposure to air, they were sealed into thin-walled glass capillaries. The peak densities of the integrated spots were measured with a Narumi Co. Ltd. microphotometer. The observed intensities were corrected for ordinary Lorentz and polarization factors and for spot extensions. Absorption and extinction corrections were not applied. A total of 786 independent reflexions, about 68% of those possible with Cu $K\alpha$ radiation, were collected.

Structure determination

Symmetry considerations

The quinone and resorcinol molecules are confined to the special positions of the unit cell, because $Z = 4$

Table 2. *Thermal parameters with standard deviations*

The thermal parameters refer to the expressions:*

$$\exp\{-B(\sin\theta/\lambda)^2\} \quad \text{or} \quad \exp\{-10^{-4}.(B_{11}h^2 + \ldots + 2B_{12}hk + \ldots)\}.$$

The B_{13} and B_{23} values of C(4) and C(7) are zero because these atoms are in special positions.

Quinone	B	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
O(1)	2·4	38 (2)	126 (13)	43 (4)	26 (5)	6 (3)	25 (6)
C(1)	1·7	21 (3)	109 (17)	31 (4)	5 (6)	0 (3)	13 (7)
C(2)	1·8	29 (3)	119 (16)	26 (4)	9 (6)	2 (3)	−4 (8)
C(3)	1·9	27 (3)	121 (18)	29 (4)	6 (6)	1 (3)	−5 (7)
H(1)	4·0 (2·2)						
H(2)	6·9 (2·0)						
Resorcinol							
O(2)	2·3	25 (2)	108 (12)	57 (4)	9 (5)	−1 (2)	26 (6)
C(4)	2·5	28 (4)	242 (32)	29 (6)	14 (11)	0	0
C(5)	2·3	24 (3)	186 (21)	40 (5)	11 (7)	3 (3)	−15 (9)
C(6)	1·7	18 (2)	104 (17)	39 (5)	4 (6)	3 (3)	10 (8)
C(7)	1·9	23 (4)	103 (23)	41 (7)	9 (8)	0	0
H(3)	3·8 (2·8)						
H(4)	3·7 (2·1)						
H(5)	5·1 (2·1)						
H(6)	2·5 (2·8)						

* The B values of the non-hydrogen atoms are the equivalent isotropic temperature factors proposed by Hamilton (1959).

is half the number of the general positions of the space group *Pnca*. According to the possible point group symmetries of the molecules, quinone and resorcinol should be located on inversion centres and twofold axes respectively.

Patterson function

The existence of an exceptionally large peak at $(\frac{1}{4},0,\frac{7}{60})$ on a three-dimensional Patterson map, together with the largest F_o value being that of the 410 reflexion, suggests that the six-membered carbon rings of quinone and resorcinol molecules are almost parallel to one another and lie approximately on the {410} planes with $\Delta z=\frac{7}{60}$. On the basis of assumed geometries of quinone and resorcinol molecules, three possible models of crystal structure compatible with these requirements were obtained. Two of them, however, were at once discarded on examination of a {410} section of the Patterson map, and from their large R values, 31 and 39 %, compared with the value 21 % for the third model, which was adopted. In the calculation of these R values, the overall temperature factor was assumed to be $B=2{\cdot}0$ Å^2, and only the one hundred strongest reflexions were taken into account.

Least-squares refinement

Full-matrix least-squares refinement was started from the above mentioned model, using all the observed

Table 3. *Observed and calculated structure factors*

The three columns give h, F_o and F_c ($\times 10$). The strongest two reflexions, 410 and 002, were not used for the least-squares refinement because they seem to be seriously affected by the extinction effect.

H 0 0		
2	117	134
4	662	869
6	96	81
8	356	-372
10	223	-229
14	41	63
18	44	-36
H 0 2		
0	1093	1315
1	349	-640
2	223	197
3	27	-29
4	129	-124
5	299	-297
6	283	254
7	47	-52
8	303	-255
9	411	411
10	310	-298
11	39	-24
12	51	-43
13	221	207
14	57	-58
15	39	-34
16	78	-07
H 0 4		
0	76	-48
1	211	194
2	746	-911
3	197	-188
4	200	-198
5	131	-125
6	232	211
8	179	186
9	71	94
10	301	-306
11	117	-120
12	57	63
13	53	58
14	197	-197
15	46	-37
16	64	-86
H 0 6		
0	83	-61
1	85	-43
2	576	-577
3	358	339
4	214	-201
5	64	-64
6	294	288
7	57	-54
8	110	113
9	71	-74
10	101	100
11	342	-344
12	129	128
14	51	64
15	46	-50
H 0 8		
0	83	59
1	60	89
3	103	90
4	126	-104
7	106	-115
8	241	267
9	94	107
10	41	-39
11	280	-290
12	395	445
13	110	117
14	64	82
H 0 10		
1	110	121
3	117	-131
4	129	-148
5	133	-151
7	108	109
8	64	74
10	76	-72
11	110	124
12	209	225
13	41	41
H 0 12		
1	124	127
2	158	-163
3	149	-155
4	51	-64
5	37	-47
6	39	-43
8	34	-35
9	106	118
10	96	-49
H 0 14		
1	69	68
2	55	54
H 1 0		
2	170	-144
4	1397	1755
6	253	243
8	188	127
12	108	-90
14	60	-60
16	145	-174
18	64	82
H 1 1		
0	482	569
1	305	-303
2	73	55
3	471	543
4	650	811
5	69	68
7	136	112
8	246	184
10	115	99
11	34	-32
12	138	-125
13	21	9
14	55	-64
15	39	49
16	44	55
18	37	-50
H 1 2		
1	269	249
2	165	-147
3	358	385
4	600	703
5	436	-418
6	349	337
7	110	70
9	230	-218
10	152	132
11	41	30
12	39	31
13	152	149
14	113	-119
15	62	-72
16	55	-67
17	53	60
18	23	-5
H 1 3		
0	239	-210
1	214	195
2	57	-39
3	179	165
4	25	29
5	393	392
6	443	-438
7	122	-101
8	117	-101
9	119	85
10	149	-121
11	161	-145
12	76	-70
13	55	54
14	73	-69
15	34	-28
17	64	82
18	46	-53
H 1 4		
1	195	187
2	535	-575
3	94	-77
4	83	-71
5	30	21
6	32	10
7	55	54
8	138	-121
9	83	-78
10	234	211
12	126	134
13	41	38
14	73	-71
15	51	-58
17	23	-31
H 1 5		
1	149	-135
2	246	-226
3	21	6
4	64	51
5	73	-48
6	436	-424
7	41	-54
8	76	-48
9	41	-40
10	62	-50
13	55	-57
15	34	-45
16	57	73
17	27	-34
H 1 6		
1	142	-121
2	452	-440
3	27	3
4	60	-60
6	271	-241
7	308	314
8	188	-178
9	67	-41
10	39	34
11	30	-38
12	60	70
15	131	-163
16	30	36
H 1 7		
0	200	-173
1	188	-160
3	135	-150
4	80	76
5	64	-40
7	188	-195
8	158	148
9	115	117
10	129	138
11	92	-79
12	85	67
13	62	61
14	41	51
15	87	-95
16	51	63
H 1 8		
0	135	-138
1	58	-38
2	43	-33
4	179	152
7	37	-37
8	296	297
11	39	32
12	142	163
13	27	32
14	37	-46
H 1 10		
1	170	172
3	110	-111
4	55	-41
5	55	68
6	30	28
7	85	-92
8	200	-213
9	53	-65
10	32	-49
13	27	37
H 1 11		
0	142	-161
1	62	72
2	51	-58
3	60	-71
5	106	115
6	55	-41
11	25	31
12	27	-36
H 1 12		
1	83	90
2	57	-57
3	69	-79
7	32	-44
9	57	-72
10	30	24
H 1 13		
0	25	35
2	46	-47
5	48	55
6	126	-144
7	41	-46
H 1 14		
1	25	-26
2	25	21
3	85	-92
H 2 0		
0	494	-486
2	37	-25
4	480	493
6	115	-120
8	615	584
10	83	74
12	319	297
14	46	-49
16	202	192
H 2 1		
1	349	-335
2	149	119
3	186	171
4	44	43
5	83	-72
6	142	-135
7	372	338
8	595	563
9	51	59
10	62	63
14	99	102
15	115	-116
16	232	-229
17	46	37
18	57	-71
H 2 2		
0	510	-510
1	260	256
2	165	-151
3	27	-7
5	246	216
6	177	-160
7	324	313
8	119	92
9	60	-58
10	149	139
11	149	140
12	51	40
14	32	28
15	96	90
16	85	73
17	53	64
H 2 3		
1	409	-403
2	526	539
3	129	109
6	202	160
7	344	311
8	202	169
9	145	144
10	119	-98
12	76	-80
13	62	-56
14	46	40
15	106	-108
H 2 4		
0	78	-64
2	287	-253
3	73	-65
4	71	63
5	193	179
6	510	-485
7	60	-47
8	53	-51
9	51	45
10	126	-97
11	34	33
13	37	41
14	83	-89
16	57	61
17	37	34
H 2 5		
2	340	301
3	138	134
4	62	49
5	103	-93
6	124	-101
7	44	-46
8	67	53
10	246	-199
12	108	-111
14	90	115
16	30	22
H 2 6		
1	41	-35
2	218	144
3	122	-113
4	119	101
6	149	-126
8	27	-26
9	57	-55
10	60	-55
11	115	103
12	53	-60
13	78	-81
14	78	-69
15	48	-50
H 2 7		
1	117	92
3	296	292
4	338	-329
5	285	-291
6	188	-174
8	62	-57
9	122	-108
10	90	-74
13	55	59
14	73	79
15	34	-26
H 2 8		
0	326	331
1	92	88
2	96	85
3	154	-141
4	365	351
5	154	166
7	64	-49
8	96	76
11	55	49
12	76	-77
14	41	-44
H 2 9		
3	115	113
4	416	-453
6	51	-57
7	57	-44
8	106	-109
11	39	-39
12	53	64
13	37	-36
H 2 10		
0	145	125
1	101	-92
3	83	103
4	158	121
5	64	65
12	90	-87
13	32	31
H 2 11		
1	71	-63
4	83	-95
5	76	86
9	73	83
H 2 12		
0	51	-53
2	90	-71
3	53	-48
4	48	-53
5	106	101
6	113	-114
7	87	-89
8	46	-51
9	27	27
H 2 13		
1	48	-64
2	108	106
4	53	65
5	30	-21
6	99	87
H 2 14		
1	44	-56
2	83	-73
3	27	-34
H 3 0		
2	71	79
4	55	-39
6	44	-20
8	51	-52
10	64	-63
12	101	-100
H 3 1		
0	232	201
1	87	78
2	39	-30
3	266	-239
4	296	-254
5	168	-172
6	71	64
7	175	167
8	234	237
10	110	-131
11	257	268
12	487	519
13	37	-27
14	64	88
15	73	84
16	67	70
H 3 2		
1	92	80
3	46	24
6	53	-52
7	67	-65
10	39	-34
11	37	34
H 3 3		
0	46	-2
1	248	201
2	593	-565
3	409	-398
4	248	-214
5	106	-112
6	152	163
7	46	39
9	142	153
10	87	-95
11	147	160
12	80	77
13	92	105
14	34	-31
15	30	31
16	55	-65
H 3 4		
1	53	-44
4	67	-63
5	44	-48
6	62	-62
7	51	-47
11	48	38
H 3 5		
0	53	59
1	133	130
2	287	-252
3	71	61
4	67	-60
5	69	-61
6	154	119
7	76	77
8	85	86
9	53	-51
10	271	-289
13	24	-20
14	172	-185
15	37	32
16	53	-70
H 3 6		
1	138	-119
3	51	-37
4	37	-38
8	30	29
9	34	42
10	34	46
11	41	25
H 3 7		
0	521	518
1	402	403
2	188	181
4	117	101
5	131	110
6	135	128
7	80	80
8	78	-87
9	126	-130
10	135	-126
11	39	-52
13	85	-88
H 3 8		
1	73	-74
4	52	45
8	39	32
9	41	46
13	23	-18
H 3 9		
0	657	709
1	101	98
4	236	216
7	92	95
8	119	-133
9	57	61
10	44	-48
12	51	-56
13	25	30
H 3 10		
3	44	52
4	57	73
8	23	29
H 3 11		
0	57	55
4	60	-61
5	46	-56
8	73	-92
9	131	153
10	53	-67
H 3 12		
1	34	34
3	46	45
H 3 13		
0	60	-80
1	64	59
2	207	-203
3	41	-47
5	34	-55
H 4 0		
0	214	-159
2	45	-42
4	257	257
6	53	53
8	402	446
10	23	20
12	156	157
14	60	-72
16	37	52
H 4 1		
1	170	164
2	152	-140
3	99	-94
4	135	-122
5	99	92
7	165	-159
8	416	-452
9	48	27
10	34	-39
14	57	-82
15	60	82
16	142	177
H 4 2		
0	227	-193
1	172	143
2	37	-16
3	106	103
4	32	31
5	138	129
6	57	-49
7	46	44
8	101	101
9	90	-85
10	34	32
15	57	69
H 4 3		
1	163	161
2	324	-299
3	141	-113
6	108	-84
7	129	-116
8	122	-126
10	67	64
11	51	39
12	60	73
13	41	48
14	39	-30
15	80	88
H 4 4		
0	73	67
1	62	68
2	106	-78
3	30	-29
5	51	40
6	299	-329
7	83	-73
8	73	-74
10	161	-158
14	51	-46
H 4 5		
1	48	-42
2	168	-155
3	152	-157
4	51	50
5	48	35
6	115	137
10	152	143
12	55	70
13	25	24
14	85	-90
H 4 6		
0	67	64
2	147	113
3	177	-159
4	51	37
5	115	-116
6	126	-134
7	57	-47
8	53	-40
9	46	-47
10	67	-61
11	62	67
13	46	-41
H 4 7		
1	32	-38
3	246	-242
4	269	263
5	165	164
6	149	152
8	55	47
9	44	38
10	57	48
13	25	-24
H 4 8		
0	170	153
1	64	60
3	145	-144
4	216	205
7	44	-46
8	106	103
9	42	42
10	48	57
11	27	29
H 4 9		
1	53	43
3	78	-74
4	322	327
8	101	104
9	25	-26
11	25	38
H 4 10		
2	53	-56
3	78	89
4	62	61
5	57	74
8	32	39
9	27	33
H 4 11		
1	60	64
4	64	73
5	41	-45
6	32	41
7	60	75
H 4 12		
0	60	-70
1	59	68
2	87	-91
4	41	-39
5	92	121
H 5 0		
4	480	-524
6	46	-59
8	51	-75
10	41	24
12	71	75
14	27	22
H 5 1		
0	250	266
1	103	-112
2	193	115
3	106	92
4	315	325
5	51	-30
6	57	-62
10	41	23
12	115	-125
13	51	46
14	39	-55
H 5 2		
1	53	-57
2	46	55
3	57	-55
4	226	-226
5	209	203
6	69	-71
9	105	106
10	51	-48
11	27	-21
13	113	-102
14	51	64
H 5 3		
0	62	-77
1	34	-33
3	51	-39
4	39	46
5	48	47
6	168	-181
7	103	-107
8	44	-37
9	37	37
10	57	-54
11	39	-40
12	57	-58
13	78	72
H 5 4		
2	188	205
4	51	60
6	60	70
8	53	49
10	76	-92
11	39	-34
12	48	-64
13	44	-51
H 5 5		
0	113	-110
1	90	-87
2	161	-164
3	48	-50
5	32	-28
6	163	-174
7	62	-78
9	46	-58
H 5 6		
1	80	90
2	188	185
4	44	47
6	115	117
7	172	-194
8	73	82
10	41	-47
12	30	-46
H 5 7		
0	129	-134
1	80	-91
2	30	-35
4	44	41
7	103	-122
8	94	110
10	110	110
11	80	-85
H 5 8		
4	51	43
7	99	-107
8	126	166
9	27	30
H 5 9		
0	92	-97
4	41	48
5	53	72
7	27	-34
8	115	155
H 5 10		
1	69	-83
3	44	54
6	39	-45
H 5 11		
0	76	-86
1	32	39
2	37	-50
H 6 0		
0	650	693
4	191	183
8	106	-119
H 6 1		
1	62	75
2	80	91
3	60	63
4	67	81
6	44	46
8	62	70
9	25	-30
H 6 2		
0	296	285
1	115	-117
5	55	-53
6	51	70
8	71	-79
9	138	157
10	106	-111
H 6 3		
1	101	113
3	101	101
7	34	-45
8	39	44
9	51	-49
10	51	49
H 6 4		
2	246	-235
4	55	-51
9	44	53
10	113	-133
H 6 5		
3	46	37
4	51	-59
7	34	-42
H 6 6		
2	184	-174
3	106	116
4	53	-59
6	67	83
7	39	-34
H 6 7		
1	41	-52
4	41	-45
6	55	-54
H 6 8		
4	41	-38
H 7 0		
2	44	-57
4	236	283
H 7 1		
0	60	65
2	48	-51
3	85	100
4	90	101
5	39	55
7	30	37
H 7 2		
2	41	-51
3	55	70
4	133	157
5	69	-64
6	62	74
7	67	78
H 7 3		
1	48	56
2	39	-47
3	87	99
5	117	128
6	94	-112
H 7 4		
2	87	-87
H 7 5		
0	48	43
2	57	-51

reflexions. Unit weights were given to all reflexions. Atomic scattering factors used were those listed in *International Tables for X-ray Crystallography* (1962). After two cycles of isotropic refinement, the R value for the observed reflexions was 19·6%. It was evident at this stage that the strongest two reflexions, 410 and 002, were seriously affected by the extinction effect; these two were not used for later refinement. Anisotropy was then introduced except for hydrogen atoms. An additional three cycles reduced the R value to 10·9%.

At the final two cycles of the refinement, the aspherical atomic scattering factors of Freeman (1959) were introduced for the oxygen atoms by the method described in previous papers (Sakurai & Ito, 1968, 1969). Only the thermal parameters of the oxygen atoms were appreciably affected by this aspherical treatment. The final R value was 10·5%. The final atomic coordinates and thermal parameters are given in Tables 1 and 2 respectively. The observed and calculated structure factors are compared in Table 3.

Discussion of the structure

Description of the crystal structure

Molecular arrangements in the crystal of quinone–resorcinol are shown in Figs. 1(*a*) and 2. In spite of the difference in the configurations of hydroxyl groups, the general pattern of the molecular arrangements in quinone–resorcinol is very similar to those in α- and β-quinhydrones, especially to that in the former [Fig. 1(*b*)].

Quinone and resorcinol molecules are alternately linked by O–H···O hydrogen bonds to form an infinite molecular chain along the ⟨$\bar{1}$40⟩ direction. These chains are packed plane-to-plane by the charge transfer force to form a molecular sheet parallel to the (001) plane. The hydrogen bond distance is 2·747 (0·006) Å, in agreement with the corresponding distances, 2·738 and 2·739 Å, found in α- and β-quinhydrones respectively. The best-fit molecular planes are

$$0{\cdot}8625x+0{\cdot}4953y+0{\cdot}1044z=0$$

and

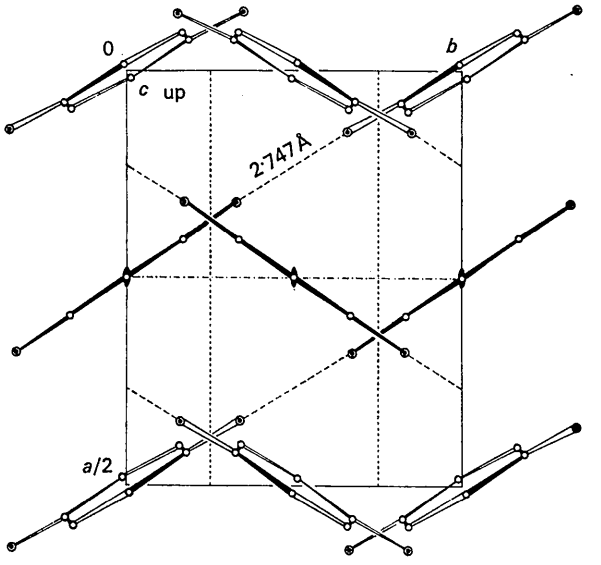
$$0{\cdot}8302x+0{\cdot}5575y=3{\cdot}041$$

for quinone and resorcinol respectively. The angle between the two molecular planes is 7·3°; the corresponding angles in α- and β-quinhydrones are 3·5 and 2·0° respectively.

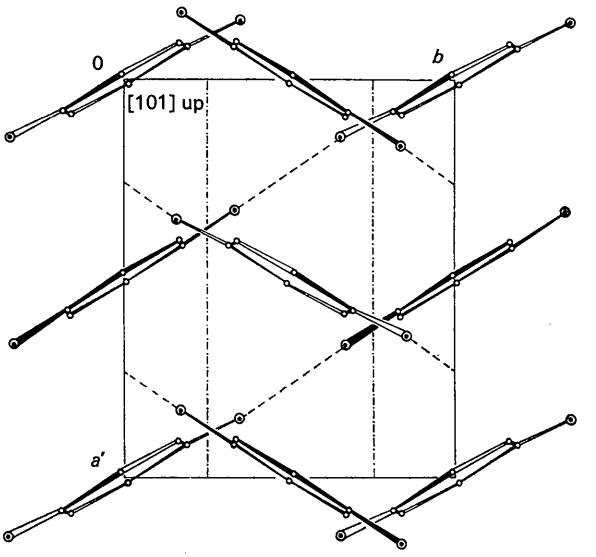
Table 4. *Densities of molecular complexes and of the component molecules*

Crystal	Density (D_x)	Reference
Quinone-resorcinol	$1{\cdot}43_6$ g.cm^{-3}	Present work
α-Quinhydrone	$1{\cdot}44_4$	Sakurai (1968)
β-Quinhydrone	$1{\cdot}48_3$	Sakurai (1965)
p-Benzoquinone	$1{\cdot}32_5$	Trotter (1960)
α-Resorcinol	$1{\cdot}28_8$	Bacon & Curry (1956)
γ-Hydroquinone	$1{\cdot}38_0$	Maartmann-Moe (1966)

The density of a molecular crystal is a useful measure of the overall molecular packing. The densities of relevant crystals are compared in Table 4. It is evident from the Table that the densities of the charge transfer complexes are considerably larger than those of the component molecules, *i.e.* the molecular packing is much denser in the complexes. The density of quinone–resorcinol is in better agreement with that of α-quin-



(*a*)



(*b*)

Fig. 1. Molecular arrangements in crystals of (*a*) quinone–resorcinol; projection along the *c* axis; (*b*) monoclinic quinhydrone; projection along the [101] axis.

hydrone than that of β-quinhydrone, probably corresponding to the higher similarity between the molecular arrangements mentioned above.

Molecular structure

The bond distances and angles are given in Table 5 and are also shown in Fig. 2. Corrections for the rigid-body librational motions were applied by the method of Cruickshank (1961).*

No extraordinary bond distances or angles were found in the molecular structures of this complex. The difference between the two C–C–OH bond angles in resorcinol (123·3 and 114·9°) is highly significant ($\delta/\sigma=$ 10·0); this is consistent with the rule that the C–C–OH bond angle on the hydrogen atom side is significantly larger than that on the other side (Maartmann-Moe, 1966; Sakurai, 1968). The C–OH distance in resorcinol, 1·378 (0·008) Å, is larger than those in α-resorcinol, $1{\cdot}33_9$ and $1{\cdot}35_9$ Å, which were determined by the two-dimensional neutron diffraction method (Bacon & Curry, 1956). This difference, however, cannot necessarily be attributed to the effect of the charge transfer interaction, because in γ-hydroquinone, in which no charge-transfer interaction exists, even larger C–OH distances (1·392 and 1·394 Å) have been observed (Maartmann-Moe, 1966). Quinone and resorcinol molecules are planar within experimental error; the deviations of the oxygen and carbon atoms from the best-fit molecular planes are less than 0·022 Å.

Charge transfer interaction

Intermolecular distances between quinone and resorcinol molecules in adjacent molecular chains are shown in Fig. 3. The perpendicular distance between the molecular planes of quinone and resorcinol is about 3·1 Å.* The shortest intermolecular C···O and C···C distances are 3·068 (0·007) and 3·208 (0·006) Å respectively, being considerably shorter than the ordinary van der Waals contact of about 3·4 Å. Such close contact between the donor and acceptor molecules is a characteristic feature of the charge transfer complex. As is evident in Fig. 3, the overlap of the six-membered carbon rings of the two molecules is very small; instead, the C–O and C=O bonds lie above and below the ring centres. This situation is also found in all the complexes of the quinhydrone type studied thus far and also in thymine–quinone complex (Sakurai & Okunuki, 1969).

Polarized crystal spectra of this complex have been investigated by Amano (1969). Intense charge-transfer bands have been observed with **a**-polarized light, whereas the crystal is almost transparent to **b**-polarized light. Simple microscopic observations indicate that the crystal absorbs **c**-polarized light to some extent. Comparison of these spectroscopic observations with the molecular orientations in the crystal (*cf.* Fig. 1) shows that the direction of the charge-transfer moment is probably parallel to the line connecting the ring cen-

* Now that the atomic parameters of quinone–resorcinol have been deduced not from the electron densities, but from the structure amplitudes, the Gaussian-breadth parameter of the librational correction q^2 is replaced by another one $q_\infty{}^2$ which is free from the series-termination effect: $q_\infty{}^2 = u_T{}^2 + u_e{}^2$, where $u_T{}^2$ is the observed mean-square amplitude of the translational motion, and $u_e{}^2$ is the Gaussian-breadth parameter of the electron distribution around the stationary atom. The latter was estimated from the analytical expression for the atomic scattering factor given by Vand, Eiland & Pepinsky (1957): $u_e{}^2 = (1{\cdot}54)^2 \,.\, a/8\pi^2$, where a is the atomic constant tabulated in the reference. The $u_e{}^2$ values for carbon and oxygen atoms are 0·012 and 0·016 Å^2 respectively.

* The perpendicular distance cannot be defined in a strict sense, because the two molecular planes are not parallel but make an angle of 7·3°.

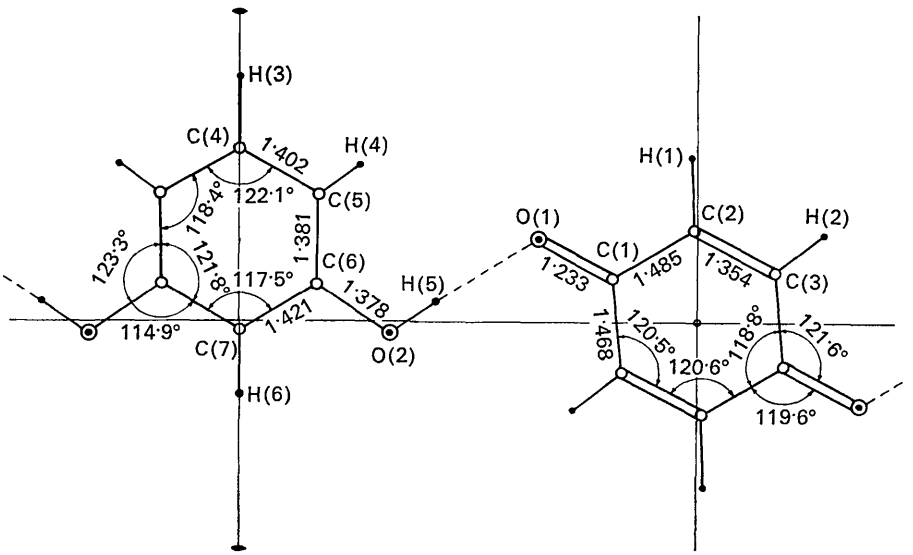


Fig. 2. Molecular chain on the (410) plane of quinone–resorcinol. The bond distances (Å) and angles are also shown.

Table 5. *Bond distances and angles with standard deviations*

Librational corrections were not applied for the hydrogen atoms.

Quinone	Distance after correction	Librational correction		Angle
O(1)–C(1)	1·233 (0·008) Å	0·001 Å	O(1) –C(1)–C(3′)	121·6 (0·6)°
			O(1) –C(1)–C(2)	119·6 (0·6)
C(1)–C(2)	1·485 (0·009)	0·005	C(2) –C(1)–C(3′)	118·8 (0·5)
C(1)–C(3′)	1·468 (0·009)	0·003	C(1) –C(2)–C(3)	120·6 (0·6)
			C(2) –C(3)–C(1′)	120·5 (0·6)
C(2)–C(3)	1·354 (0·009)	0·003	C(1) –C(2)–H(1)	120 (5)
			C(3) –C(2)–H(1)	120 (5)
C(2)–H(1)	1·12 (0·09)		C(2) –C(3)–H(2)	117 (4)
C(3)–H(2)	1·11 (0·08)		C(1′)–C(3)–H(2)	121 (4)
Resorcinol				
O(2)–C(6)	1·378 (0·008)	0·002	O(2)–C(6)–C(5)	123·3 (0·6)
			O(2)–C(6)–C(7)	114·9 (0·6)
C(4)–C(5)	1·402 (0·008)	0·002	C(5)–C(4)–C(5′)	122·1 (0·8)
C(5)–C(6)	1·381 (0·009)	0·004	C(4)–C(5)–C(6)	118·4 (0·6)
C(6)–C(7)	1·421 (0·008)	0·003	C(5)–C(6)–C(7)	121·8 (0·6)
			C(6)–C(7)–C(6′)	117·5 (0·7)
O(2)–H(5)	0·90 (0·08)		C(6)–O(2)–H(5)	114 (5)
			C(5)–C(4)–H(3)	119 (1)
C(4)–H(3)	1·13 (0·13)		C(4)–C(5)–H(4)	120 (5)
C(5)–H(4)	0·98 (0·08)		C(6)–C(5)–H(4)	118 (5)
C(7)–H(6)	0·99 (0·12)		C(6)–C(7)–H(6)	121 (1)

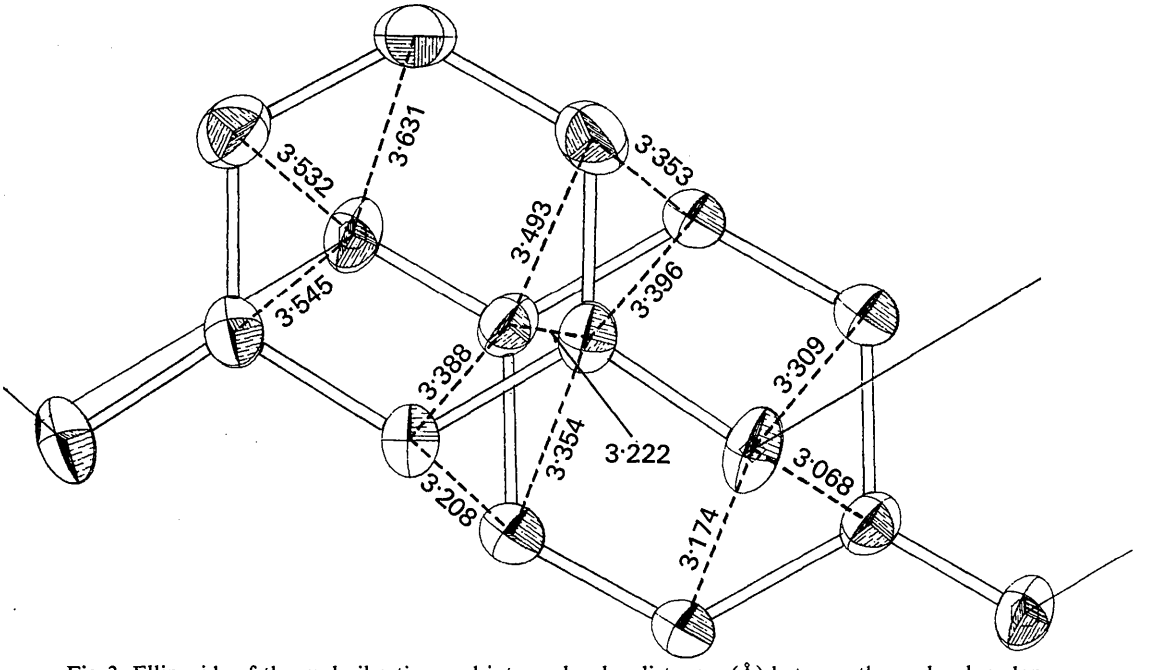


Fig. 3. Ellipsoids of thermal vibration and intermolecular distances (Å) between the molecular planes.

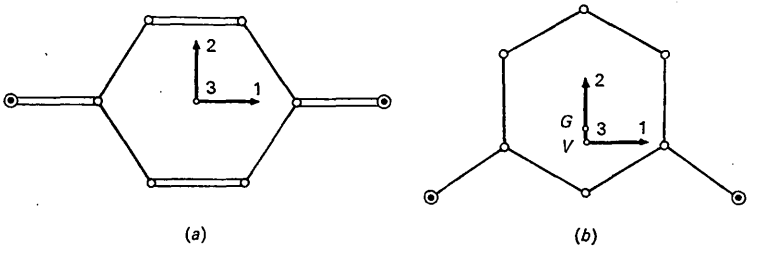


Fig. 4. Axes of the rigid-body vibration. (*a*) Quinone. (*b*) Resorcinol. The points *V* and *G* are the centres of vibration and gravity of the molecule respectively.

Table 6. *Translational and librational tensors of the rigid-body vibration with standard deviations*

(T in 10^{-3} Å^2 and Ω in degrees^2)

The 12 and 23 elements of resorcinol are zero because the molecule is in a special position.

	T_{11}	T_{22}	T_{33}	T_{12}	T_{13}	T_{23}
Quinone	17 (1)	17 (1)	15 (3)	0 (1)	3 (1)	2 (1)
Resorcinol	18 (1)	22 (1)	23 (2)	0	1 (1)	0
	Ω_{11}	Ω_{22}	Ω_{33}	Ω_{12}	Ω_{13}	Ω_{23}
Quinone	30 (6)	16 (2)	6 (1)	2 (3)	2 (3)	3 (1)
Resorcinol	15 (3)	2 (2)	11 (1)	0	7 (2)	0

Table 7. *Observed and calculated vibrational tensors of the individual atoms* (10^{-3} Å^2 units)

	U_{11}		U_{22}		U_{33}		U_{12}		U_{13}		U_{23}	
Quinone	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.
O(1)	15	17	29	30	48	48	−2	0	4	3	−5	−5
C(1)	16	17	23	21	24	24	2	0	1	3	−2	0
C(2)	21	20	17	18	32	32	0	2	2	1	2	1
C(3)	23	20	19	18	30	30	0	−2	1	2	2	2
Resorcinol												
O(2)	18	20	39	41	29	28	8	6	2	0	−4	−4
C(4)	34	32	19	22	40	41	0	0	−8	−8	0	0
C(5)	27	24	27	27	33	32	−6	−6	−5	−3	0	4
C(6)	18	18	26	27	21	23	2	0	0	1	−4	0
C(7)	17	20	28	22	27	25	0	0	1	0	0	0

tres (Anex & Parkhurst, 1963), and definitely not perpendicular to the molecular planes.

Thermal vibrations

The thermal ellipsoids of individual atoms in quinone–resorcinol are shown in Fig. 3. These were transformed into the rigid-body vibration of the molecule (Cruickshank, 1956). The z coordinate of the centre of vibration of the resorcinol molecule was included in the variable parameters of the least-squares treatment; it was found to be 0·053. Axes of molecular vibration are shown in Fig. 4. The most probable values of the translational and librational tensors, **T** and **Ω** respectively, are shown in Table 6. The observed and calculated vibrational tensors **U** of the individual atoms are compared in Table 7; these are in satisfactory agreement. The translational motions of both quinone and resorcinol molecules are isotropic within experimental error. Significant anisotropies are observed in the librational motions of both molecules. The relations between these anisotropies and the nature of the force fields around the molecules will be discussed elsewhere.

The numerical calculations were performed on the HITAC 5020 computer of the Computer Centre of the University of Tokyo and on the OKITAC 5090H computer of this Institute, with a universal crystallographic computation program system, *UNICS* (Sakurai, Ito, Iwasaki, Watanabe & Fukuhara, 1967). This work was supported in part by a Scientific Research Grant of the Ministry of Education.

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