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The Crystal and Molecular Structure of 1,5-Dihydroxyanthraquinone

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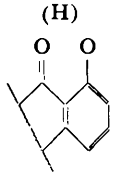
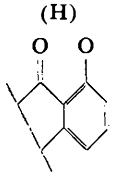
Crystals of 1,5-dihydroxyanthraquinone are monoclinic with two molecules in a unit cell of dimensions $a=15\cdot755$, $b=5\cdot308$, $c=6\cdot003$ Å, $\beta=93°37'$, space group $P2_1/a$. The structure was solved by Fourier methods and refined in three dimensions with anisotropic thermal parameters, using differential syntheses. The final R value was 13·3 % and the mean coordinate standard deviation 0·004 Å. The molecule forms a strong asymmetric intramolecular hydrogen bond. Electron delocalization across the quinonoid ring, as gauged by the structural parameters, appears minimal. The molecular packing is tight.

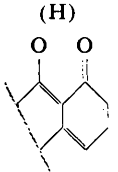
The hydroxyanthraquinones offer an interesting problem in hydrogen bonding, in that when substituted in the α position they can form intramolecular bonds, but in the β position intermolecular bonds only. The melting points of the former compounds are characteristically lower (Table 1), although 1,5-dihydroxyanthraquinone is an exception. Various spectroscopic investigations have been reported (Peters & Sumner, 1953; Hadzi & Sheppard, 1954; Bloom, Briggs & Cleverley, 1959). The spectra of the α-substituted compounds confirm the formation of an intramolecular bond, and are interpreted in terms of contributing structures, such as (I), (II), and (III).



(I)



(II)



(III)

The spectra are consistent with a strong hydrogen bond, but the proton is thought to be asymmetrically placed between the two oxygen atoms and firmly attached to only one of them. The possibility of occasional proton tunnelling between two potential minima in the bond could not, however, be excluded.

Table 1. *Melting points of some anthraquinone derivatives*

Derivative	m.p.
1-Hydroxy	190°C
2-Hydroxy	302
1,8-Dihydroxy	191
1,4-Dihydroxy	194
1,5-Dihydroxy	280
1,2-Dihydroxy	290
2,6-Dihydroxy	>330

The present three-dimensional crystallographic study of 1,5-dihydroxythraquinone was undertaken to provide information on the over-all structure of the molecule, to attempt to describe further the extent and influence of hydrogen bonding upon the structure, and to explain the abnormal melting point of these crystals.

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Experimental

Crystal data

1,5-dihydroxyanthraquinone, $C_{14}H_8O_4$, M.Wt. 240·2
Monoclinic:
$a=15{\cdot}755\pm0{\cdot}010$, $b=5{\cdot}308\pm0{\cdot}005$, $c=6{\cdot}003\pm0{\cdot}005$ Å, $\beta=93°37'\pm4{\cdot}5'$
$Z=2$, $V=501{\cdot}0$ Å^3
$D_m=1{\cdot}570$, $D_x=1{\cdot}595$ g.cm^{-3}
Absent spectra: $h0l$ when h odd, $0k0$ when k odd.
Space group $P2_1/a$ (C_{2h}^5)
Linear absorption coefficient (Cu $K\alpha$), $\mu=11{\cdot}36$ cm^{-1}
Crystal habit: Orange-red monoclinic prisms bounded by (100) (major) and (102) (minor) faces. Interfacial angle 52°.
Optical properties: Crystals biaxial positive; strong pleochroism, high dispersion.
Refractive indices $\alpha=1{\cdot}720\pm0{\cdot}005\perp[102]$
$\beta=1{\cdot}748\pm0{\cdot}005\perp[010]$
$\gamma=1{\cdot}960\pm0{\cdot}010\perp\alpha\beta$ plane
Optic axial angle, $2V=44°$.

Crystals (m.p. 279°C) were obtained from a chloroform–ligroin solvent. The unit-cell parameters were found with a rotating crystal camera using the Straumanis back-reflexion photographic technique and the least-squares procedure of Hess (1951).

Intensity data

The dimensions of the crystals used in this investigation were 0·50 × 0·25 × 0·05 mm (approximately). Equi-inclination multiple-film Weissenberg photographs were taken with Cu $K\alpha$ radiation about all three axes. In this way the reciprocal lattice zones $0kl$–$9kl$, $h0l$–$h3l$ and $hk0$ were recorded. The $h0l$ and $hk0$ data were used to solve the structure and initiate the refinement; three-dimensional refinement was then carried out with the data collected from the a- and b-axis photographs. All intensities were estimated by visual comparison with a calibrated intensity scale and corrected for Lorentz and polarization effects. Absorption corrections were not made. The three-dimensional refinement was carried out on a total of 1050 reflexions which the photography made accessible, and of which 865 were of measurable intensity. The unobserved reflexions were included at half the minimum observable value. Empirical corrections for secondary extinction (Pinnock, Taylor & Lipson, 1956) were made for 31 of the most intense reflexions in the course of the structure refinement.

Solution and refinement of the structure

There are two molecules in the unit cell of 1,5-dihydroxyanthraquinone and the centres of mass of these molecules must be located at inversion centres. The positions (0,0,0) and ($\frac{1}{2}$,$\frac{1}{2}$,0) were chosen. If $G_0(\mathbf{S})$ and $G_0'(\mathbf{S})$ are the Fourier transforms of these two molecules respectively, each referred to its own centre of mass as origin, then in standard notation (Lipson & Taylor, 1958) the Fourier transform of the contents of the unit cell referred to the unit cell origin is given by

$$G_1(\mathbf{S})=G_0(\mathbf{S})+G_0'(\mathbf{S})\exp 2\pi i(\tfrac{1}{2}\mathbf{a}+\tfrac{1}{2}\mathbf{b})\,.\,\mathbf{S}\,.$$

In the $h0l$ projections the a axis is halved and there is only one molecule in the unit area. Because the molecule is centrosymmetrical its transform is real, so that in the $h0l$ reciprocal lattice section

$$G_1(\mathbf{S})=2G_0(\mathbf{S})=4\sum_{n=1}^{N/2} f_n\cos 2\pi\mathbf{r}_n\,.\,\mathbf{S}$$

N = number of atoms in one molecule.

The idealized transform (Knott, 1940) of the expected molecule was calculated assuming standard bond lengths, and the orientation of the molecule was determined by superposition of the $h0l$ section of the weighted reciprocal lattice. The transform showed pronounced pseudo-hexagonal symmetry such that three different orientations gave a reasonable fit, but the correct one was clearly preferred when the smaller terms were considered. The signs of $F(h0l)$ were read from the transform and used in a Fourier synthesis, which clearly revealed the projection of the structure. This was then refined by successive difference syntheses. The atomic scattering factors used were those of Berghuis, Haanappel, Potters, Loopstra, MacGillavry & Veenendaal (1955). The structure factor program contained provision for only one overall temperature factor. The initial atom coordinates for the [001] projection were obtained from a projected molecular model in the appropriate orientation, and were then refined in the same way.

The three-dimensional refinement of the structure (excluding hydrogen atoms) was commenced with the use of a consistent set of atom coordinates derived from the studies of the projected structure, and the mean thermal parameter of the two projections (2·9 Å^2) applied to the atoms individually. The refinement was carried out on an IBM 7070 computer using the differential synthesis method of Shiono (1962). All the observed structure amplitudes were included in the refinement, and the unobserved amplitudes were included at half the minimum observable value. During the six cycles of refinement using individual isotropic thermal parameters R fell from 0·30 to converge at 0·196. (The R index quoted in these results is $R=\sum||F_o|-|F_c||/\sum|F_o|$; the unobserved reflexions were included with the observed reflexions in calculations of R). At this stage the coordinate standard deviations were all $<0{\cdot}007$ Å and the coordinate shifts in the sixth cycle less than half this value. Following four cycles of refinement with anisotropic thermal parameters the reliability was 0·156. The three hydrogen atoms attached to carbon atoms were then included in the structure factor calculations on the assumption that they lay in the molecular plane distant 1·09 Å from their conjoint carbon atoms. For the hydrogen atoms

Table 2. *Observed and calculated structure factors* (× 10)

Spectra asterisked were corrected for secondary extinction; those denoted < were not observed and are recorded as $F(\text{obs})_{\min}$.

	h00	
4	187	-167
6	166	170
8	142	125
10	166	170
12	74	6
14	176	201
16	30	-37
18	30	-37
	h01	
-20	47	54
-18	67	-66
-16	89	74
-14	471*	444
-12	172	168
-10	< 23	30
-8	24	-17
-6	43	-29
-4	367*	371
-2	331*	-322
0	79	116
2	505*	494
4	131	-137
6	10	-16
8	426*	-436
10	304	-323
12	46	41
14	33	-25
16	51	-40
18	56	-49
20	< 12	-11
	h02	
-18	44	28
-16	67	-56
-14	41	38
-12	< 26	15
-10	79	-70
-8	90	75
-6	498*	-487
-4	662*	-656
-2	50	-75
0	28	-2
2	107	-133
4	289*	-307
6	38	-25
8	151	104
10	131	-142
12	82	-72
14	49	52
16	< 30	10
18	49	-51
	h03	
-18	105	-116
-16	49	-43
-14	< 34	-4
-12	< 32	-4
-10	105	-90
-8	20	-25
-6	77	60
-4	93	-60
-2	37	26
0	65	72
2	20	26
4	67	-61
6	111	109
8	42	38
10	42	-32
12	< 30	22
14	< 34	27
16	< 24	3
18	53	-73
	h04	
-18	35	-27
-16	27	22
-14	71	66
-12	71	-51
-10	49	-43
-8	126	137
-6	52	50
-4	102	-90
-2	76	72
0	57	69
2	194	-241
4	185	-210
6	34	35
8	31	-31
10	63	62
12	53	53
14	34	-33
	h05	
-16	< 14	-20
-14	< 24	8
-12	73	75
-10	143	-139
-8	158	-170
-6	39	-37
-4	32	-40
-2	126	148
0	< 14	6
2	94	-97
4	77	66
6	38	-36
8	25	-17
10	< 32	-29
12	54	48
14	200	219
	h06	
-12	44	-34
-10	65	42
-8	25	80
-6	89	31
-4	82	-43
-2	49	52
0	305	363
2	100	98
4	25	-23
6	< 30	34
8	< 28	17
10	57	46
	h07	
-10	< 32	19
-8	11	-7
-6	17	67
-4	76	-39
-2	41	88
0	37	3
2	90	[illegible]
4	< 24	3
6	< 18	5
	h10	
1	303*	318
2	279*	-291
3	93	-95
4	135	-127
5	738*	-284
6	389*	-457
7	132	-183
8	166*	-177
9	24	-18
10	44	-6
11	18	8
12	54	-53
13	44	-37
14	55	-24
15	67	56
16	166	-195
17	109	128
18	61	-67
19	< 16	11
	h11	
-19	40	-44
-18	< 20	-5
-17	36	-35
-16	79	81
-15	61	48
-14	99	-95
-13	116	123
-12	98	-99
-11	16	9
-10	77	76
-9	141	-152
-8	291*	-333
-7	171	-189
-6	275*	-326
-5	19	10
-4	81	-108
-3	117	106
-2	20	-25
-1	186*	-203
0	87	-104
1	219*	197
2	969*	-1012
3	506*	667
4	317*	-290
5	121	113
6	119	126
7	91	-79
8	157	-159
9	78	-63
10	46	-32
11	77	60
12	28	-14
13	24	70
14	26	14
15	56	-45
16	26	-4
17	48	35
18	74	-76
19	59	65
	h12	
-19	< 14	-6
-18	50	-49
-17	30	47
-16	< 20	6
-15	62	-54
-14	< 24	4
-13	90	76
-12	216	-277
-11	194	219
-10	130	-144
-9	96	93
-8	< 13	-2
-7	< 31	-4
-6	65	-47
-5	73	-44
-4	91	84
-3	47	-48
-2	87	-82
-1	155	178
0	39	34
1	147	-163
2	90	58
3	152	164
4	44	-51
5	120	117
6	28	22
7	60	-47
8	18	-7
9	< 20	-1
10	115	121
11	109	-125
12	138	147
13	67	-54
14	< 22	-14
15	19	-23
16	63	-67
17	67	-68
18	18	-15
19	10	-4
	h13	
-18	56	53
-17	< 18	10
-16	< 20	6
-15	< 24	-20
-14	70	-67
-13	< 20	-4
-12	71	75
-11	55	53
-10	26	18
-9	56	31
-8	67	-57
-7	93	-82
-6	< 13	6
-5	158	153
-4	174	-197
-3	277*	335
-2	120	-120
-1	56	67
0	118	-131
1	206	-243
2	109	-218
3	102	-82
4	47	-36
5	99	100
6	92	-83
7	< 17	-4
8	< 20	9
9	42	39
10	47	41
11	77	-79
12	< 20	22
13	< 20	-7
14	< 20	-11
15	39	-36
	h14	
-17	48	-59
-16	86	86
-15	25	-15
-14	53	51
-13	72	-57
-12	97	-92
-11	109	-107
-10	74	-70
-9	36	-33
-8	31	9
-7	72	-46
-6	23	16
-5	44	53
-4	29	26
-3	44	-35
-2	114	-116
-1	35	-26
0	61	54
1	34	20
2	19	10
3	65	-58
4	77	-62
5	30	28
7	48	-41
8	36	-32
9	41	33
10	59	58
11	142	155
12	139	160
13	70	69
14	< 20	1
15	< 18	-21
16	< 14	-12
	h15	
-16	< 8	-2
-15	49	-42
-14	< 18	-15
-13	51	40
-12	< 20	-12
-11	43	36
-10	< 20	8
-9	36	-33
-8	54	55
-7	53	-51
-6	54	-100
-5	47	37
-4	62	71
-3	180	224
-2	209	251
-1	120	106
0	79	75
1	< 14	-14
2	50	-9
3	< 20	-2
4	75	30
5	75	79
6	39	-34
7	10	110
8	4	-44
9	17	-25
10	< 13	16
11	< 14	63
12	31	11
	h16	
-13	< 12	-3
-12	7	21
-11	15	20
-10	17	-42
-9	< 20	18
-8	52	50
-7	23	-22
-6	57	-51
-5	56	-51
-4	21	-16
-3	< 2	-23
-2	< 22	69
-1	57	73
0	< 14	-3
1	< 12	89
2	< 26	-42
3	< 23	-1
4	26	28
5	< 6	-59
6	23	-87
7	66	-58
8	51	-40
9	< 12	-23
10	< 16	-5
11	< 14	[illegible]
	h17	
-9	35	-40
-8	74	75
-7	63	-61
-6	57	-59
-5	24	-20
-4	23	-22
-3	< 14	0
-2	< 10	6
-1	16	-69
0	< 20	-15
1	136	-152
2	86	89
3	56	-62
4	15	14
5	14	2
6	26	-37
	h20	
0	222*	[illegible]
1	176	-172
2	40	-34
3	151	165
4	65	-54
5	132	-118
6	143	-147
7	80	-59
8	69	-65
9	179	108
10	126	-130
11	136	158
12	25	-25
13	19	-32
14	< 22	-17
15	< 20	4
16	< 22	14
17	< 20	13
18	47	59
19	13	-19
	h21	
-19	36	43
-18	26	-22
-17	< 22	-21
-16	< 22	3
-15	19	-21
-14	66	-66
-13	48	45
-12	< 20	-47
-11	72	66
-10	79	-69
-9	15	-26
-8	50	-48
-7	57	-33
	h22	
-7	86	-99
-6	86	-33
-5	236*	239
-4	275*	267
-3	290*	308
-2	111	-121
-1	[illegible]	6
0	21	-10
1	131	134
2	147	143
3	166	-175
4	181	183
5	71	-58
6	77	-73
7	126	127
8	77	67
9	32	-62
10	79	[illegible]
11	< 20	-51
12	61	-72
13	82	-46
14	67	-57
15	53	-16
16	< 26	-16
17	< 22	-16
18	30	96
	h23	
-18	17	-45
-17	24	22
-16	[illegible]	-50
-15	< 24	7
-14	47	-47
-13	60	70
-12	106	106
-11	132	-135
-10	132	130
-9	96	-83
-8	82	-77
-7	92	87
-6	70	59
-5	39	-25
-4	151	150
-3	58	-41
-2	11	9
-1	213*	-302
0	215*	-331
1	161	-142
2	114	-117
3	56	-16
4	317*	328
5	403*	-460
6	230	224
7	100	-87
8	< 15	5
9	41	43
10	22	-18
11	41	-40
12	< 22	-13
13	< 2	10
14	< 26	3
15	79	-73
16	41	-33
17	< 20	-8
18	< 14	-2
	h24	
-18	24	33
-17	< 18	19
-16	23	25
-15	113	-112
-14	80	-73
-13	47	-40
-12	97	-83
-11	54	-46
-10	117	141
-9	212	-255
-8	172	197
-7	22	-32
-6	61	69
-5	57	-45
-4	83	-77
-3	61	-24
-2	52	-47
-1	114	105
0	55	57
1	133	-129
2	65	-7
3	21	-20
4	80	-43
5	47	50
6	64	-5
7	< 17	177
8	166	232
9	188	150
10	124	43
11	48	-52
12	53	41
13	41	-63
14	63	90
15	84	11
16	< 20	[illegible]
	h25	
-17	< 8	-4
-16	37	-33
-15	69	59
-14	< 20	9
-13	22	-16
-12	< 24	-2
-11	24	24
-10	27	-20
-9	76	-75
-8	24	-24
-7	48	49
-6	160	154
-5	245	302
-4	188	225
-3	59	49
-2	51	-38
-1	99	100
0	118	-132
1	150	180
2	14	-6
3	85	73
4	98	84
5	74	64
6	25	15
7	77	-15
8	52	-19
9	88	83
10	88	89
11	63	107
12	< 24	63
13	35	-9
14	[illegible]	-39
15	[illegible]	85
	h26	
-15	37	47
-14	51	-47
-13	63	57
-12	44	-39
-11	31	32
-10	47	39
-9	21	56
-8	37	-28
-7	66	-45
-6	57	47
-5	45	-46
-4	83	85
-3	63	53
-2	< 14	12
-1	< 16	-11
0	45	34
1	62	-83
2	90	-97
3	91	-1
4	35	-21
5	25	-41
6	< 20	19
7	42	-44
8	23	-30
9	33	-13
	h27	
-12	24	-17
-11	67	-44
-10	71	-57
-9	99	-106
-8	41	-32
-7	< 10	5
-6	55	-58
-5	25	23
-4	27	-26
-3	55	-62
-2	21	-21
-1	71	-74
0	62	-62
1	< 16	-7
2	< 18	3
3	< 26	3
4	24	-27
5	61	-61
6	30	-47
7	56	-57
8	< 20	-15
9	42	43
10	33	-38
	h31	
-5	31	41
-4	45	-46
-3	35	32
-2	35	-32
-1	< 10	-5
0	33	-16
1	13	22
2	43	43
3	15	-40
4	49	30
	h32	
1	77	16
2	47	-31
3	10	-6
4	47	45
5	64	63
6	32	20
7	70	59
8	16	-13
9	48	-33
10	17	-4
11	110	-131
12	22	-39
13	37	-39
14	< 20	-5
15	33	30
16	17	2
17	37	-43
	h33	
-18	36	-28
-17	17	-14
-16	< 18	-6
-15	49	48
-14	< 20	2
-13	< 22	-5
-12	< 22	7
-11	47	-46
-10	< 18	3
-9	35	48
-8	< 15	-10
-7	96	96
-6	< 13	1
-5	15	-32
-4	15	2
-3	297*	-333
-2	111	-118
-1	77	-64
0	49	-51
1	77	76
2	30	18
3	171	-163
4	54	34
5	61	-43
6	44	45
7	47	-25
8	39	-21
9	24	-16
10	22	15
11	74	-62
12	66	53
13	161	-157
14	< 26	-3
15	< 22	-9
16	< 20	6
	h34	
-17	87	-121
-16	15	-24
-15	48	-38
-14	40	-34
-13	< 20	2
-12	< 22	10
-11	46	-49
-10	62	64
-9	24	15
-8	65	64
-7	99	-91
-6	53	-49
-5	< 15	14
-4	54	32
-3	44	-30
-2	137	139
-1	273	-273
0	31	28
1	87	-74
2	14	-2
3	68	-52
4	54	32
5	196	221
6	92	94
7	267	312
8	114	119
9	68	-57
10	18	-13
11	25	19
12	22	18
13	65	56
14	36	39
15	16	14
16	24	24
	h35	
-16	45	45
-15	39	-54
-14	27	21
-13	33	-30
-12	21	15
-11	95	-100
-10	17	-18
-9	181	212
-8	60	63
-7	258*	325
-6	121	132
-5	55	-41
-4	< 16	4
-3	58	40
-2	16	-3
-1	102	108
0	50	40
1	134	130
2	65	50
3	79	52
4	42	33
5	95	-53
6	42	-40
7	30	308
8	1.2	-31
9	48	204
10	34	24
11	< 26	-47
12	< 20	-12
13	[illegible]	-11
14	25	-16
15	62	-53
16	32	-36
	h41	
-14	17	-13
-13	71	68
-12	30	90
-11	39	25
-10	36	33
-9	63	-57
-8	83	-83
-7	184	226
-6	57	-61
-5	140	169
-4	15	6
-3	19	19
-2	< 18	-6
-1	25	-21
0	45	-38
1	155	-162
2	91	-104
3	47	-35
4	49	-45
5	< 26	-6
6	< 15	3
7	50	-38
8	68	-79
9	26	13
10	74	-74
11	52	-49
12	32	-25
13	< 10	-7
14	< 14	8
	h42	
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-11	57	-51
-10	43	-32
-9	17	-21
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-2	47	-41
-1	16	12
0	< 14	6
1	51	-55
2	150	26
3	24	-164
4	48	-23
5	< 18	-47
6	< 18	-9
7	21	18
8	10	12
9	17	-21
10	< 10	-8
	h43	
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-9	< 9	-31
-8	< 14	5
-7	< 16	5
-6	< 14	3
-5	19	-13
-4	< 16	-3
-3	25	-19
-2	24	19
-1	25	19
0	16	16
1	13	15
2	21	19
3	31	-20
4	43	41
5	16	7
6	33	28
7	36	41
8	< 12	10
	h44	
0	176	-76
1	57	-58
2	26	17
3	42	35
4	93	-75
5	119	-116
6	109	-110
7	38	24
8	16	18
9	[illegible]	-53
	h45	
-9	41	44
-8	74	-82
-7	56	52
-6	35	20
-5	25	-11
-4	44	-24
-3	114	-113
-2	27	-4
-1	26	-19
0	13	-6
1	17	-74
2	134	143
3	102	226
4	163	150
5	14	15
6	30	-20
7	25	-20
8	16	30
	h46	
-9	143	169
-8	41	25
-7	30	-18
-6	17	-10
-5	< 20	90
-4	93	48
-3	56	-16
-2	17	16
-1	158	171
0	26	-21
1	61	43
2	17	-58
3	67	-56
4	82	71
5	178	193
6	122	121
7	111	101
8	16	-15
9	< 28	-18
	h47	
-9	97	112
-8	71	65
-7	70	67
-6	< 10	-6
-5	53	40
-4	34	-31
-3	48	-48
-2	77	-49
-1	94	-109
0	114	-148
1	81	69
2	77	-76
3	23	18
4	54	-50
5	34	-31
6	45	-53
7	85	-84
8	41	27
9	122	-135
	h50	
-9	< 28	19
-8	62	-57
-7	94	-99
-6	48	43
-5	144	-165
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-3	30	30
-2	33	-38
-1	36	-38
0	54	-57
1	109	-110
2	52	-56
3	48	-37
4	33	31
5	< 20	5
6	17	14
7	[illegible]	-5
	h51	
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-7	20	21
-6	< 11	7
-5	28	-59
-4	112	127
-3	70	-64
-2	45	49
-1	< 14	7
0	< 14	13
1	< 12	10
2	7	11
3	79	67
4	16	12
5	29	31
6	33	36
7	< 14	-8
8	29	-32
	h52	
-5	39	-45
-4	17	-9
-3	21	-19
-2	28	31
-1	21	20
0	< 10	-9
1	< 6	-10
3	27	28
	h53	
1	122	131
2	141	164
3	75	74
4	< 16	12
5	78	-76
6	54	55
7	30	27
8	36	35
9	41	52
	h54	
-9	69	-62
-8	66	70
-7	23	-11
-6	45	41
-5	44	36
-4	42	45
-3	25	40
-2	< 14	11
-1	48	10
0	14	-49
1	127	134
2	134	148
3	102	98
4	44	37
5	< 16	10
6	85	-96
7	62	51
8	59	-53
	h55	
-9	< 28	30
-8	36	-35
-7	47	-54
-6	38	37
-5	76	-81
-4	70	-70
-3	75	-70
-2	55	-52
-1	< 14	15
0	17	-11
1	40	-28
2	38	-35
3	48	-43
4	39	-44
5	29	-34
6	48	-54
7	56	-53
8	22	19
	h56	
-9	10	-31
-8	36	-33
-7	51	-57
-6	28	28
-5	< 20	-8
-4	22	-18
-3	48	-43
-2	95	-111
-1	56	-56
0	86	-31
1	64	-54
2	62	79
3	15	-38
4	< 20	-4
5	48	-45
6	43	-39
7	< 16	6
	h57	
-9	< 10	-2
-8	16	-14
-7	17	-17
-6	22	24
-5	< 20	12
-4	< 16	13
-3	< 14	-3
-2	28	29
-1	< 14	10
0	23	17
1	51	48
2	55	51
3	27	-19
4	57	58
5	44	-37
6	28	-20
7	38	-36
	h58	
-4	33	-40
-3	70	84
-2	55	-63
-1	< 10	5
0	25	29
1	< 10	6
2	6	3
3	< 8	11
4	< 4	2
	h60	
0	167	215
1	61	60
2	63	47
3	30	30
4	29	-30
5	34	-35
6	< 14	9
7	38	-35
	h61	
-7	47	-54
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1	134	-131
2	66	55
3	70	-59
4	36	-39
5	< 20	-13
6	< 10	-6
7	13	12
	h62	
-6	64	-78
-5	25	-21
-4	75	-82
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-2	17	-13
-1	11	8
0	17	20
1	17	-18
2	< 10	15
3	42	-38
4	39	-43
5	15	-18
6	< 10	4
	h63	
-6	< 6	-3
-5	29	37
-4	34	-33
-3	< 10	42
-2	25	13
-1	30	24
0	14	34
1	< 10	9
2	18	4
3	35	-12
4	< 10	-37
5	[illegible]	-10

McWeeny's (1951) scattering factor curves were used, together with isotropic thermal parameters of 3·0 Å^2: but neither these parameters nor the positional parameters were refined. After an additional four cycles of refinement the R value was 0·133, the standard deviations of the carbon and oxygen atoms being less than 0·005 Å. Following Cruickshank (1956), four further cycles of anisotropic refinement were carried out on the reflexions for which $\sin\theta > 0{\cdot}6$. The R value for these data fell from 0·146 to 0·141, and the coordinate standard deviations converged to a mean value of 0·004 Å. The mean parameter shifts in the final cycle were 0·0002 Å for the atom coordinates and 0·024 Å^2 for the thermal parameters. At this point the refinement was concluded. Observed reflexion amplitudes and final calculated structure factors are given in Table 2.

Final atom coordinates and thermal parameters were taken from the fourth differential synthesis calculated for the high Bragg angle data (Tables 3 and 4; Fig. 1 explains the atom numbering scheme used). Bond lengths and bond angles for the 1,5-dihydroxyanthraquinone molecule and their standard deviations were estimated by the methods of Ahmed & Cruickshank (1953) (bond length) and Darlow (1960) (bond angles) (Tables 5 and 6). Corrections to the bond lengths for the rotational oscillation of the molecule were not applied. The best mean plane through the carbon and oxygen atoms was found to be

$$-0{\cdot}5224x' + 0{\cdot}6342y' - 0{\cdot}5700z' = 0$$

(where x', y', z' are atomic coordinates in Å referred to orthonormal axes a, b, c'). The mean deviation from this plane was 0·009 Å. Neglecting the oxygen atoms, the carbon atoms lay in the plane

$$-0{\cdot}5214x' + 0{\cdot}6346y' - 0{\cdot}5704z' = 0$$

with a mean deviation of 0·006 Å. The distances of the oxygen atoms from this plane were 0·023 Å [O(1)] and 0·020 Å [O(2)] (Table 7). Close intermolecular approaches were also calculated, and some of these are shown in Fig. 2.

The 'residual structure' remaining after the conclusion of the structure refinement was revealed by calculating a three-dimensional difference Fourier synthesis, for which only the non-hydrogen atoms were included in the calculated structure amplitudes. The section through this synthesis in the plane of the molecule is shown in Fig. 3.

Discussion

The dimensions of the quinonoid group in 1,5-dihydroxyanthraquinone are listed in Table 8, together with those from other molecules whose structures have been studied with comparable precision. It may be seen that the lengths of the quinonoid carbonyl bonds C(7)–O(2) and of the adjacent bonds C(7)–C(6) are remarkably constant, as are the bond angles at the carbonyl carbon. The bond C(7)–O(2) has the same length in these compounds as the carbonyl bond in acetone

Table 3. *Fractional coordinates and standard deviations* × 10^4

	x/a	y/b	z/c
C(1)	1120 ± 3	−0267 ± 9	−3363 ± 7
C(2)	1880 ± 3	1430 ± 11	−3315 ± 8
C(3)	1966 ± 3	3233 ± 9	−1621 ± 8
C(4)	1396 ± 3	3397 ± 9	−0005 ± 8
C(5)	0725 ± 3	1728 ± 8	−0033 ± 7
C(6)	0616 ± 3	−0175 ± 9	−1712 ± 7
C(7)	−0103 ± 3	−1935 ± 8	−1741 ± 7
O(1)	1160 ± 3	−1937 ± 8	−5047 ± 6
O(2)	−0195 ± 2	−3558 ± 7	−3161 ± 6
H(2)*	2344	1309	−4596
H(3)	2501	4528	−1578
H(4)	1474	4789	1330

* H(2) is bonded to C(2) *etc.*

Table 4. *Anisotropic thermal parameters* B_{ij} × 10^2 (Å^2)

	B_{11}	B_{22}	B_{33}	B_{12}	B_{23}	B_{31}
C(1)	205	210	176	36	−8	13
C(2)	193	301	224	4	27	50
C(3)	221	256	306	−39	25	22
C(4)	191	206	217	−50	−24	−2
C(5)	151	155	199	−5	10	−5
C(6)	167	211	192	31	−4	1
C(7)	194	164	206	−8	−50	−15
O(1)	293	277	248	−28	−86	102
O(2)	273	281	285	−67	−159	74

Table 5. 1,5-*Dihydroxyanthraquinone bond lengths and standard deviations*

C(1)–C(2)	1·399 ± 0·007 Å
C(2)–C(3)	1·397 ± 0·007
C(3)–C(4)	1·365 ± 0·007
C(4)–C(5)	1·379 ± 0·006
C(5)–C(7′)	1·495 ± 0·006
C(5)–C(6)	1·429 ± 0·006
C(6)–C(7)	1·469 ± 0·006
C(6)–C(1)	1·395 ± 0·006
C(1)–O(1)	1·343 ± 0·006
C(7)–O(2)	1·214 ± 0·005

Table 6. 1,5-*Dihydroxyanthraquinone bond angles and standard deviations*

C(1)–C(2)–C(3)	119·66 ± 0·93°
C(2)–C(3)–C(4)	121·53 ± 0·97
C(3)–C(4)–C(5)	119·23 ± 0·92
C(4)–C(5)–C(7′)	118·69 ± 0·80
C(7′)–C(5)–C(6)	119·98 ± 0·78
C(4)–C(5)–C(6)	121·33 ± 0·85
C(5)–C(6)–C(7)	121·05 ± 0·82
C(6)–C(7)–O(2)	121·17 ± 0·85
C(6)–C(7)–C(5′)	118·97 ± 0·77
O(2)–C(7)–C(5′)	119·87 ± 0·83
C(5)–C(6)–C(1)	118·12 ± 0·82
C(7)–C(6)–C(1)	120·80 ± 0·83
C(6)–C(1)–O(1)	123·63 ± 0·88
C(6)–C(1)–C(2)	120·08 ± 0·87
O(1)–C(1)–C(2)	116·28 ± 0·83

Table 7. *Distances of atoms from the mean planes* (Å)

	All atoms	Carbon atoms
C(1)	0·005 Å	0·008 Å
C(2)	0·000	0·005
C(3)	−0·008	−0·004
C(4)	−0·004	−0·001
C(5)	−0·004	−0·003
C(6)	−0·015	−0·014
C(7)	−0·006	−0·006
O(1)	0·020	0·023
O(2)	−0·020	−0·020

and in acetaldyhyde (1·215 ± 0·005 Å: Sutton, 1965), and may be described as a normal double bond. Similarly, the bond length C(1)–O(1) is listed in Table 9 with the length of other single bonds between an oxygen and an sp_2-hybridized carbon atom, and it may be seen that all are in agreement with the value 1·34 ± 0·02 Å suggested by Lide (1962) for such a bond. It appears then that any electron delocalization in 1,5-dihydroxyanthraquinone from the carbonyl group into the ring system is too small to have any effect on the carbon–oxygen bond lengths.

The mean bond length of the carbon–carbon bonds in the benzenoid rings is 1·394 Å, which is the same (within the limits of error) as the bond length in the benzene ring (1·397 Å; Sutton, 1965). However, the bonds C(3)–C(4) and C(5)–C(6) both show significant deviations from the mean. The fractional weights of the three resonance contributors (I), (II), and (III) which give the best agreement with the observed bond lengths are 0·47, 0·50 and 0·03, showing that resonance between the two chemically equivalent contributors is virtually complete.

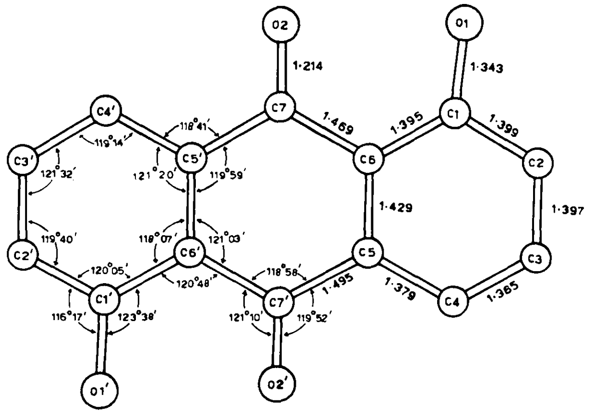

Fig. 1. The 1,5-dihydroxyanthraquinone molecule. Atom nomenclature used and calculated bond lengths (Å) and bond angles are included (hydrogen atoms omitted).

The hydrogen atoms

The section through the final difference Fourier synthesis in the plane of the molecule (Fig. 3) contains the highest positive peaks observed (0·59, 0·55, 0·55, 0·45 e.Å^{-3}). These peaks undoubtedly represent the positions of the four electrons associated with each of the hydrogen atoms H(2), H(3), H(4) and H(1) respectively. There are a further six peaks greater than 0·30 e.Å^{-3} of which one is a subsidiary peak close to the site of H(1), and the others are randomly placed. The synthesis also contains thirteen negative peaks higher than −0·30 e.Å^{-3}, of which the largest is −0·78 e.Å^{-3}. Eight of these peaks surround atom sites; four are randomly placed; and the centre of the quinonoid ring has a density of −0·43 e.Å^{-3}.

These negative peaks may indicate the presence of an unresolved systematic error in the data, such as that due to absorption. The effect of this on the structure parameters would be small and confined mainly to the thermal parameters. Any absorption effects have been minimized by excluding low angle data from the final refinement cycles but none-the-less the thermal parameters have been treated with reserve and no quantitative conclusions have been based upon them.

The difference synthesis shows that the electron peaks for atoms H(2), H(3) and H(4) occur at approximately 0·9 Å from their respective carbon atoms. This is in general agreement with the short carbon–hydrogen bond lengths measured in many organic structures by X-ray means (Jensen, 1962) and from which it is believed that the hydrogen electron migrates in the bond towards its conjoint carbon atom. The position of the electron of the hydrogen H(1) in the hydrogen bond is much less certain but it appears to be asymmetrically located in the bond, and slightly displaced from the line joining O(1) and O(2). The major and minor positive peaks in the synthesis in the region of the hydrogen bond indicate that although the electron is in the main involved in the H(1)–O(1) bond, it is

Table 8. *Bond lengths and angles in some quinonoid compounds**

	C(7)–O(2)	C(6)–C(7)	C(5)–C(6)	$\sigma(l)$	C(6)–C(7)–C(5′)	$\sigma(\theta)$	Reference
p-Benzoquinone	1·222 Å	1·477 Å	1·322 Å	0·007 Å	117°48′	37′	Trotter (1960)
Anthraquinone†	1·224	1·478	1·372	0·013	117 29	—	Murty (1960)
1,5-Dihydroxy-anthraquinone†	1·214	1·469‡	1·429	0·006	118 58	46′	Present work

* The nomenclature used is given in Fig. 1.
† Values uncorrected for rotational oscillation.
‡ Value for C(5)–C(7′), 1·495 Å.

Table 9. *Some C(sp_2)–O bond lengths*

Molecule	C(1)–O(1)	$\sigma(l)$	Reference
α-Resorcinol	1·349 Å	0·020 Å	Bacon & Curry (1956)
Formic acid*	1·343	0·003	Kwei & Curl (1960)
Tetrachlorohydroquinone	1·349	0·019	Sakurai (1962)
Salicylic acid*	1·358	0·004	Sundaralingam & Jensen (1965)
1,5-Dihydroxyanthraquinone	1·343	0·005	Present work

* The C–O hydroxyl bond is taken.

also attracted to the slightly electron deficient carbonyl oxygen atom and spends part of its time in the vicinity of this atom, as previously suggested (Hadzi & Sheppard, 1954).

The intramolecular hydrogen bond

The measured C(1)–O(1) and C(7)–O(2) bond lengths show that the hydrogen bond between the two oxygen atoms is far from symmetric in form, and this is sub-

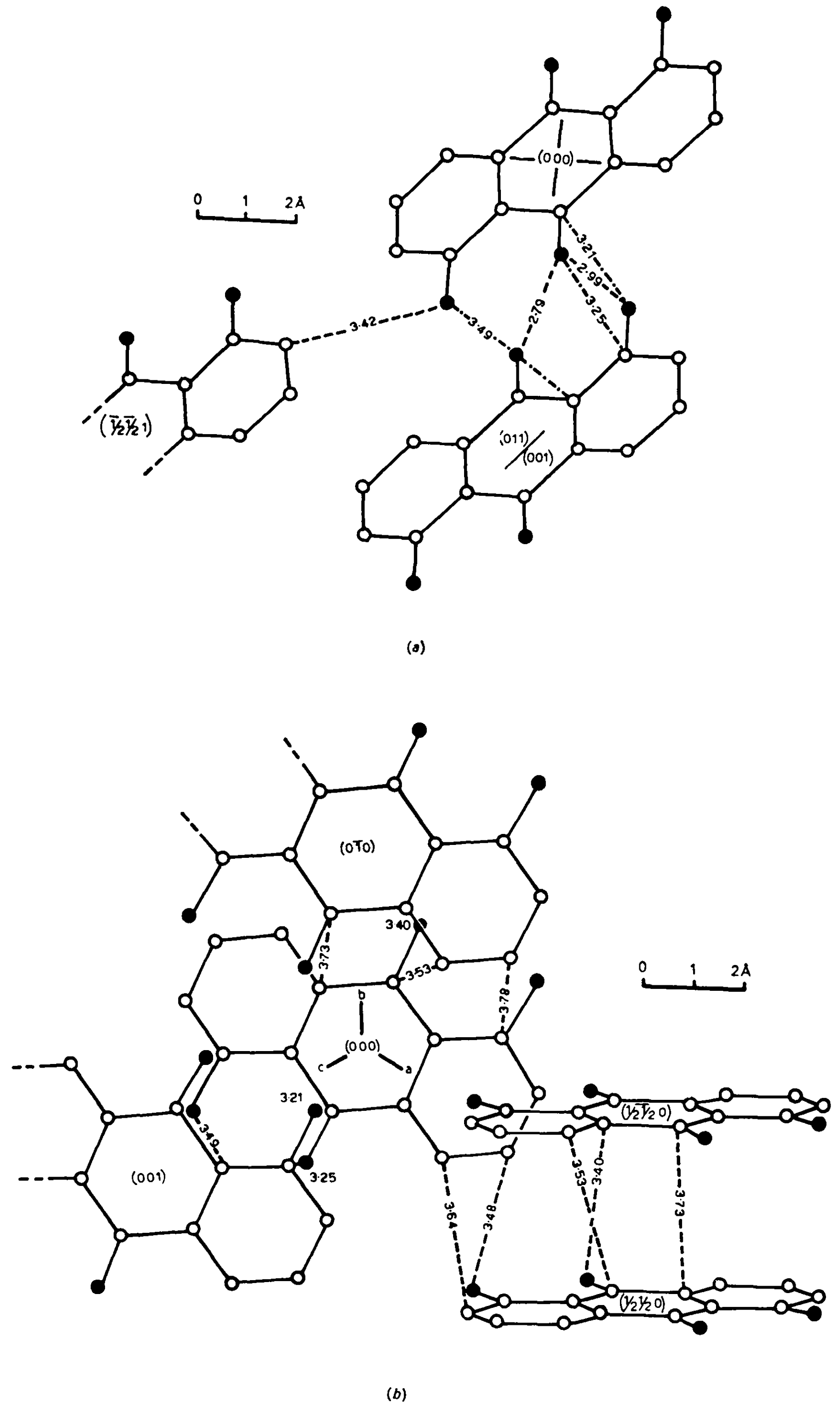

Fig. 2. Packing diagrams: (*a*) viewed along [010]; (*b*) viewed perpendicular to the plane of the molecule centred at (0,0,0). Open circles are carbon atoms, shaded circles oxygen atoms. Distances are in Å; in (*a*), chained lines refer to distances between the molecules centred at (0,0,0) and (0,0,1), dashed lines to distances between the molecules centred at (0,0,0) and (0,1,1).

stantiated by the information from the difference synthesis concerning the electron of the hydrogen H(1). Moreover, the oxygen atoms, in seeking their most favoured positions energetically, have moved apart, and this is in the direction opposite to that indicated for the formation of a symmetrical hydrogen bond from an idealized 1,5-dihydroxyanthraquinone molecule having the measured bond lengths but undistorted (120°) bond angles at C(1) and C(7). The O(1)···O(2) separation in this idealized molecule would be 2·50 Å; the separation measured for 1,5-dihydroxyanthraquinone is 2·62 Å; the separation in symmetrically hydrogen-bonded potassium hydrogen maleate is 2·44 Å (Darlow & Cochran, 1961).

The deviations of individual atoms from the mean molecular plane through the carbon and oxygen atoms are significant (χ^2 test); however, deviations of the carbon atoms from the mean plane of the carbon atoms alone are probably not so (probability $\leq 0{\cdot}03$; C(4) is the only atom in doubt). Thus the two oxygen atoms in addition to being repelled in the molecular plane are displaced from this plane by significant amounts in opposite directions, *viz.* +0·020 Å [O(1)] and −0·020 Å [O(2)].

Details of the intramolecular hydrogen bond in 1,5-dihydroxyanthraquinone are very similar to those reported for salicylic acid (Sundaralingam & Jensen, 1965).

Intermolecular approaches

The intermolecular approach distances (Fig. 2) between the two molecules centred at (0,0,0) and (0,1,1) are remarkably short: O(2)···O(2′) being 2·79 Å and O(1)···O(2′) 2·99 Å. These distances compare with the long intermolecular hydrogen bonds of up to 2·92 Å found in crystalline tartaric acid (Stern & Beevers, 1950). Although these distances in 1,5-dihydroxyanthraquinone are not less than the van der Waals diameter of an oxygen atom (2·8 Å approximately; Pauling, 1960), they are notably less than those found in other purely benzenoid or quinonoid compounds such as *p*-benzoquinone (≥3·63 Å; Trotter, 1960). A set of close intermolecular approaches similar to those of 1,5-dihydroxyanthraquinone has been found in naphthazarin (Pascard-Billy, 1962), where O(1)···O(2′) is 3·11 Å, O(2)···O(2′) 3·05 Å (in the nomenclature of the present paper). It appears therefore that there is an unusually strong intermolecular interaction in both naphthazarin and in particular in 1,5-dihydroxyanthraquinone, and that this interaction is mediated by the hydrogen bonds. In 1,5-dihydroxyanthraquinone, the separation of the planes containing the molecules at (0,0,0) and (0,1,1) is only 0·052 Å and therefore it appears that the proton of the atom H(1) may participate in the interactions among O(1), O(2) and O(2′) (the latter two of which are electron deficient), and thus stabilize this very close intermolecular approach. (The X in Fig. 3 indicates the projected position of O(2′) onto the plane of the molecule containing O(1) and O(2).) A neutron diffraction study of 1,5-dihydroxyanthraquinone would enable this suggestion to be more thoroughly examined.

The shortest C···O non-bonded distances indicate a tighter overall packing of the molecules than is evident in many similar structures such as *p*-benzoquinone, 9-anthraldehyde (Trotter, 1959), 9,10-anthrahydroquinone dibenzoate (Iball & Mackay, 1962), but the equivalent distances in naphthazarin are similar. The C···C approaches in 1,5-dihydroxyanthraquinone (3·48, 3·51, 3·53, 3·64 Å) are similar to those of other aromatic compounds containing polar groups.

The atomic thermal parameters also attest to considerable constriction of the thermal motions of the atoms in the crystal. Table 10 contains the derived atomic anisotropic thermal parameters (U_{ij}) referred to the orthogonal axes **a**, **b**, and **c**′. These tensor elements may be compared with the corresponding elements for the atoms of anthracene (Cruickshank, 1956; here the U_{ij} are referred to the molecular axes).

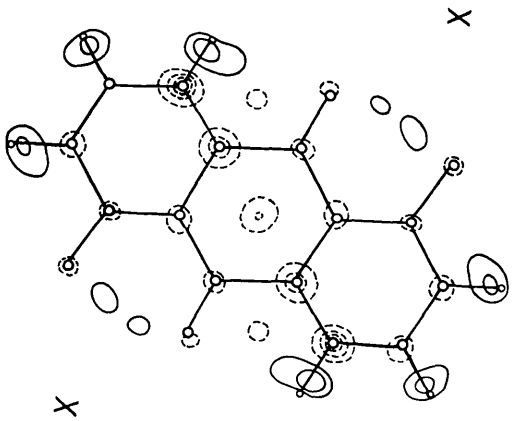

Fig. 3. The final difference Fourier synthesis: the section through the molecular plane. Contour interval is 0·25 Å^{-3}; full lines are positive; dashed lines are negative; zero is omitted. For an explanation of X see text.

Table 10. *Derived anisotropic thermal parameters* (U_{ij}) × 10^{-2} Å^2

	U_{11}	U_{22}	U_{33}	U_{12}	U_{23}	U_{31}
C(1)	2·6	2·7	1·9	0·5	0·1	0·0
C(2)	2·4	3·8	1·6	0·0	0·3	0·5
C(3)	2·8	3·2	3·3	−0·5	0·4	0·1
C(4)	2·4	2·6	2·8	0·6	−0·3	−0·2
C(5)	1·9	2·0	2·7	0·0	0·1	−0·2
C(6)	2·1	2·7	2·4	0·4	0·1	−0·1
C(7)	2·5	2·1	3·0	−0·1	−0·6	−0·3
O(1)	3·7	3·5	0·6	−0·4	−1·1	1·1
O(2)	3·5	3·6	1·8	−0·8	−2·0	0·7

It is evident from these intermolecular approach distances and from the anisotropic thermal parameters that very strong forces exist between molecules in the crystals, and that these forces indicate the origin of the uncharacteristically high melting point of these crystals.

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Hydrogen Bond Studies. X. The Crystal Structure of Ammonium Hydrogenperoxide

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The crystal structure of NH_4OOH has been determined from three-dimensional single-crystal X-ray data, recorded at −36 and −170°C. The data indicate that the same structure occurs at both temperatures. The structure belongs to the space group $P2_1/c$ and has four molecules in each unit cell. The unit-cell dimensions at −160°C are: $a = 6{\cdot}580$, $b = 6{\cdot}767$, $c = 6{\cdot}143$ Å; $\beta = 121{\cdot}73°$. The assignment of the hydrogen atoms to the bonds indicates clearly that the structure contains ammonium ions and hydrogenperoxide ions and the compound in the solid state should accordingly be written as NH_4OOH. The hydrogenperoxide ions are linked by short hydrogen bonds (2·54 Å) to form parallel infinite chains. The ammonium ions form links between these chains (hydrogen bonds of length 2·72 and 2·85 Å) giving a three-dimensional network.

Introduction

The melting point diagram for the system NH_3–H_2O_2 has been studied by Maas & Hatcher (1922) and Mironov (1959). The diagram has a very pronounced maximum which corresponds to a compound with the composition $NH_3.H_2O_2$, melting at 24·5°C. According to Mironov there is also a compound with the composition $2NH_3.H_2O_2$.

From the Raman spectrum (Simon & Kriegsmann, 1955) and the infrared spectrum (Knop & Giguère, 1959) of the crystalline 1:1 compound it has been concluded that the solid contains ammonium and hydrogenperoxide ions. In the liquid state, however, the Raman spectra recorded by Simon & Marchand (1950) and Simon & Uhlig (1952) gave no indication that such ions exist to a measurable extent.

The present account concerns an X-ray investigation of the crystalline compound $NH_3.H_2O_2$.

Experimental

Two series of investigations were undertaken with two different crystals.

In one instance dry ammonia was distilled into a weighed capillary containing a known amount of water-free hydrogen peroxide (see below). The capillary was sealed off and then weighed again to determine the