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The Crystal Structure of Catechol

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The crystal structure of catechol (*o*-dihydroxybenzene) has been determined from three-dimensional X-ray diffraction data. The *R* value over 912 structure amplitudes was 5·8 %. The mean C–C bond length is 1·385 Å, C–O 1·372 Å and the hydrogen-bond length 2·801 Å.

Introduction

The unit-cell dimensions of catechol (*o*-dihydroxybenzene) were first given, erroneously, by Caspari (1926), and later, approximately correctly, by Kitaigorodskii (1947). Although the structures of the isomeric resorcinol (Robertson, 1936; Robertson & Ubbelohde, 1938) and quinol (Palin & Powell, 1947, 1948; Powell & Riesz, 1948; Kitaigorodskii, 1949; Powell, 1950; Wallwork, 1956; Lee & Wallwork, 1959) have both been studied extensively by X-ray crystallographers, no detailed work appears to have been carried out on catechol. For this reason, it was decided to work out the structure and a short account of the results was presented to the Fifth Congress of the International Union of Crystallography at Cambridge (Brown, 1960).

Experimental

A sample of commercial catechol (m.p. 105°; Found, C 65·6, H 5·5%. $C_6H_6O_2$ requires C 65·4, H 5·5%), while consisting to a large extent of dark grey and black powder, was found to contain a number of well-formed, almost colourless, crystals. After checking the axial directions and perfections of some of these, a suitable specimen was cut to a reasonable size with a razor blade and was used for obtaining all the X-ray data. Rotation and Weissenberg photographs were taken about the principal axes; measurement of high order reflexions gave the following unit cell dimensions:

$$a = 10{\cdot}941,\ b = 5{\cdot}509,\ c = 10{\cdot}069\ \text{Å};\ \beta = 119{\cdot}0°.$$

Absent reflexions showed the space group to be unambiguously $P2_1/a$, and the specific gravity determined by flotation in sodium iodide solution was 1·371, agreeing with the calculated value of 1·374 required for four molecules of $C_6H_4(OH)_2$ per unit cell.

Weissenberg photographs for intensity measurements were taken about **a** (zero layer only) and **b** (zero and four layers). Nine films were exposed at each camera setting, three films in each pack, with exposure times of 18 hours, 2 hours and 13 minutes, in order to cover as wide a range of intensities as possible. The spots were estimated by comparison with a calibrated time-exposed film strip, and the usual correction factors were applied. Scaling between the layers about **b** was done by comparison with corresponding spots on the **a** photograph, and the final adjustment of the structure amplitudes to the absolute scale was done on the computer.

Table 1. *Atomic parameters*

The values of B are defined by the expression

$$\exp\left[-\tfrac{1}{4}(h^2a^{*2}B_{11}+2hka^*b^*B_{12}+\ldots)\right]$$

used in the structure amplitude calculations.

	x/a	y/b	z/c	B_{11}	B_{22}	B_{33}	B_{12}	B_{23}	B_{13}
C(1)	0·1105	0·3682	0·1761	2·22	2·53	2·93	0·36	0·38	1·31
C(2)	−0·0139	0·3556	0·1811	2·26	2·94	3·09	0·24	0·25	1·38
C(3)	−0·0360	0·5045	0·2778	2·99	4·32	3·59	0·11	−0·44	1·95
C(4)	0·0662	0·6711	0·3683	4·00	4·13	3·55	0·08	−0·54	1·86
C(5)	0·1893	0·6837	0·3624	3·95	4·32	3·83	−0·94	−0·80	1·66
C(6)	0·2125	0·5301	0·2662	2·75	3·77	3·90	−0·35	−0·06	1·72
O(1)	0·1251	0·2137	0·0767	2·33	3·73	3·73	−0·32	−0·56	1·95
O(2)	−0·1180	0·2009	0·0888	2·37	4·47	4·84	−0·82	−1·70	2·25
H(1)	0·2242	0·2468	0·0813	Mean isotropic $B = 3{\cdot}58$					
H(2)	−0·1208	0·0410	0·0249						
H(3)	−0·1325	0·4948	0·2823						
H(4)	0·0488	0·7892	0·4435						
H(5)	0·2687	0·8116	0·4329						
H(6)	0·3090	0·5401	0·2618						

Mean standard deviation of positional coordinates, 0·0022 Å.
Mean standard deviation of thermal parameters, 0·10.

Table 2. *Observed and calculated structure amplitudes*

H	K	L	F(OBS)	F(CAL)
0	0	1	34.5	+35.7
0	0	2	35.9	-34.5
0	0	3	10.5	+9.2
0	0	4	21.8	-20.9
0	0	5	11.2	-10.6
0	0	6	11.7	-10.6
0	0	7	11.8	-11.0
0	0	8	3.7	-3.1
0	0	9	10.6	-11.1
0	0	11	11.8	+11.2
2	0	-12	0.5	+0.5
2	0	-10	3.2	-3.6
2	0	-9	1.9	-1.9
2	0	-8	7.1	-7.2
2	0	-7	6.5	+5.5
2	0	-6	26.7	+26.2
2	0	-5	5.8	-5.2
2	0	-4	11.4	-11.1
2	0	-3	2.4	-3.2
2	0	-2	24.8	-25.0
2	0	-1	40.6	+39.7
2	0	0	19.4	+18.9
2	0	1	16.1	-17.5
2	0	2	3.8	+1.9
2	0	3	20.3	-20.4
2	0	5	13.3	+12.3
2	0	6	4.6	-4.8
2	0	7	1.9	-1.8
2	0	8	4.1	-3.9
2	0	9	3.7	-4.4
2	0	10	5.8	+6.1
4	0	-12	5.9	-6.7
4	0	-11	0.8	-0.6
4	0	-10	1.4	+1.1
4	0	-9	2.4	-2.5
4	0	-8	5.4	+4.7
4	0	-7	22.9	+24.6
4	0	-6	21.8	+23.8
4	0	-5	8.7	+8.4
4	0	-4	12.3	+12.8
4	0	-3	18.0	+18.9
4	0	-2	36.2	-38.0
4	0	-1	62.8	-63.6
4	0	0	23.7	-24.7
4	0	1	14.1	-15.5
4	0	2	23.0	-22.7
4	0	3	6.7	-6.4
4	0	4	19.5	+19.1
4	0	5	11.8	+11.1
4	0	6	1.4	+1.2
4	0	7	4.5	+4.7
4	0	8	3.7	+4.2
6	0	-13	2.4	-2.9
6	0	-12	1.9	+1.0
6	0	-11	1.8	+2.3
6	0	-10	4.8	+5.1
6	0	-9	10.6	+10.0
6	0	-8	11.8	-10.9
6	0	-7	12.6	-13.2
6	0	-6	5.2	+6.0
6	0	-4	13.8	+15.4
6	0	-3	6.4	+6.5
6	0	-2	25.2	-24.9
6	0	-1	2.4	-2.6
6	0	0	1.9	-1.4
6	0	1	0.9	+0.8
6	0	2	8.0	+8.1
6	0	3	5.4	-4.6
6	0	4	3.9	-3.1
6	0	5	1.8	+1.7
6	0	6	1.2	+1.2
6	0	7	5.1	+5.1
8	0	-12	2.9	+3.1
8	0	-11	4.5	+4.1
8	0	-10	16.7	+16.4
8	0	-9	3.1	-3.5
8	0	-8	30.8	-30.6
8	0	-7	9.8	-10.5
8	0	-6	7.8	-8.0
8	0	-5	11.9	-12.1
8	0	-4	1.6	-1.4
8	0	-3	2.8	-2.4
8	0	-2	8.9	+8.9
8	0	-1	9.2	+9.1
8	0	0	13.1	+12.7
8	0	1	30.8	+31.9
8	0	2	3.9	+4.9
8	0	3	16.6	-15.9
8	0	4	3.4	-3.1
8	0	5	1.4	-1.5
10	0	-10	1.7	+1.3
10	0	-9	5.0	-4.6
10	0	-8	2.4	-2.4
10	0	-7	1.0	-1.0
10	0	-6	1.9	+2.0
10	0	-5	9.8	+9.6
10	0	-4	2.4	-2.7
10	0	-3	7.6	-7.6
10	0	-2	0.9	+0.9
10	0	-1	1.4	+0.7
10	0	0	8.3	+8.0
10	0	1	6.0	+5.8
10	0	2	5.4	-5.1
10	0	3	2.4	-2.7
12	0	-11	7.3	-8.0
12	0	-10	1.5	+1.5
12	0	-9	6.7	+6.5
12	0	-8	2.8	+3.0
12	0	-7	5.8	+6.2
12	0	-6	13.3	+14.1
12	0	-5	8.5	+8.7
12	0	-4	2.7	-3.4
12	0	-3	2.6	-2.6
12	0	-2	0.7	-0.7
12	0	-1	7.9	-7.8
12	0	0	9.8	-9.0
14	0	-7	3.1	-3.5
14	0	-6	3.7	-4.1
14	0	-5	3.1	+3.2
0	1	1	22.4	-21.5
0	1	2	94.2	-94.8
0	1	3	21.1	-22.5
0	1	4	8.9	-8.5
0	1	5	14.6	-13.5
0	1	6	2.9	+2.9
0	1	7	6.4	-5.5
0	1	8	1.0	+1.3
0	1	9	13.0	+12.7
0	1	10	3.7	+4.1
0	1	11	2.4	+2.3
1	1	-11	3.3	-3.8
1	1	-10	2.7	+3.0
1	1	-9	3.8	+4.5
1	1	-8	1.0	-0.8
1	1	-7	1.7	-1.5
1	1	-6	8.8	-8.3
1	1	-5	6.4	-5.7
1	1	-4	5.4	-5.1
1	1	-3	7.7	+7.4
1	1	-2	42.7	+43.2
1	1	-1	18.0	-17.7
1	1	0	43.6	-44.5
1	1	1	37.9	+39.1
1	1	2	30.2	+30.4
1	1	3	5.2	-4.3
1	1	4	4.3	-4.1
1	1	5	6.0	-6.9
1	1	6	4.9	-4.9
1	1	7	5.4	-5.3
1	1	8	1.4	+2.9
1	1	9	7.8	+7.8
1	1	10	2.9	-2.1
2	1	-12	0.7	-0.9
2	1	-10	2.8	-2.8
2	1	-9	1.9	+1.5
2	1	-8	10.5	+10.8
2	1	-7	1.8	+1.6
2	1	-6	3.1	+2.4
2	1	-5	5.3	-4.8
2	1	-4	22.0	-22.9
2	1	-3	14.9	+13.6
2	1	-2	10.2	+9.4
2	1	-1	2.9	-3.4
2	1	0	12.6	+12.4
2	1	1	34.3	-34.9
2	1	2	8.6	-8.1
2	1	3	16.0	+16.3
2	1	4	3.1	-3.9
2	1	5	3.4	+3.1
2	1	6	2.9	-1.6
2	1	7	5.4	-5.7
2	1	8	4.4	+5.3
2	1	9	2.8	+3.4
2	1	10	1.4	+1.2
3	1	-12	1.2	+1.1
3	1	-11	1.7	-1.9
3	1	-10	3.7	-4.2
3	1	-9	2.7	+2.5
3	1	-8	8.2	+7.7
3	1	-7	5.3	-5.2
3	1	-6	7.8	-7.0
3	1	-5	18.9	+19.9
3	1	-4	13.2	+12.6
3	1	-3	19.6	-19.8
3	1	-2	9.5	-10.2
3	1	-1	1.3	+1.0
3	1	0	10.1	-10.8
3	1	1	17.7	-17.9
3	1	2	7.7	+6.5
3	1	3	14.6	+14.2
3	1	4	7.2	-6.4
3	1	5	6.5	-5.5
3	1	6	6.1	+5.2
3	1	7	2.7	+2.5
4	1	-11	3.2	+3.8
4	1	-10	6.5	+7.0
4	1	-9	7.4	+7.5
4	1	-8	8.2	+7.6
4	1	-7	5.4	+5.8
4	1	-6	2.2	-2.0
4	1	-5	15.5	-15.8
4	1	-4	30.9	-30.8
4	1	-3	36.4	-38.6
4	1	-2	24.6	-25.1
4	1	-1	17.6	-17.6
4	1	0	3.8	+3.4
4	1	1	16.5	+16.3
4	1	2	23.1	+22.8
4	1	3	17.6	+16.9
4	1	4	11.1	+10.8
4	1	5	6.1	+6.1
4	1	6	1.9	-1.4
4	1	7	2.5	-2.8
4	1	8	2.1	-2.5
4	1	9	1.8	-2.2
5	1	-12	1.6	+1.7
5	1	-11	2.4	-2.7
5	1	-10	1.9	-1.9
5	1	-8	1.3	+1.4
5	1	-7	1.0	+1.9
5	1	-6	5.1	+5.1
5	1	-5	11.2	+11.2
5	1	-4	8.6	-8.0
5	1	-3	13.0	-13.2
5	1	-2	11.3	+12.4
5	1	-1	2.9	+3.4
5	1	0	17.3	-18.1
5	1	1	8.3	-7.8
5	1	2	2.8	+2.4
5	1	4	1.4	-1.5
5	1	5	3.4	+3.8
5	1	6	4.5	+5.3
5	1	7	1.7	-2.1
5	1	8	2.0	-2.5
6	1	-12	1.5	+1.4
6	1	-11	5.4	+5.8
6	1	-10	4.5	-4.3
6	1	-9	7.5	-7.2
6	1	-8	2.1	-1.7
6	1	-7	5.5	-5.2
6	1	-6	10.6	+10.0
6	1	-5	8.5	+8.1
6	1	-4	13.4	-12.9
6	1	-3	1.5	-1.3
6	1	-2	9.2	-8.9
6	1	-1	1.0	-0.9
6	1	0	16.7	+16.3
6	1	1	2.0	-1.7
6	1	2	2.9	-2.6
6	1	3	1.4	+1.6
6	1	4	1.4	-0.8
6	1	5	3.7	+4.3
6	1	6	1.7	+1.8
6	1	7	2.1	-2.7
7	1	-12	2.6	+2.9
7	1	-11	2.6	+3.0
7	1	-10	7.1	-6.7
7	1	-9	5.3	-5.2
7	1	-8	13.6	+12.9
7	1	-7	2.3	+2.3
7	1	-6	13.6	-14.2
7	1	-5	5.8	-5.5
7	1	-4	2.8	-2.1
7	1	-3	3.6	+3.2
7	1	-2	6.2	+6.5
7	1	-1	7.5	+8.1
7	1	0	6.7	+7.2
7	1	1	9.2	-9.9
7	1	2	6.7	-6.1
7	1	3	8.6	+8.2
7	1	4	2.3	+2.4
7	1	5	2.3	-2.3
7	1	6	1.6	-1.6
8	1	-12	3.7	+4.9
8	1	-11	2.8	-2.9
8	1	-10	12.5	-12.9
8	1	-9	8.6	-9.9
8	1	-8	14.9	-14.4
8	1	-6	16.4	+17.5
8	1	-5	6.5	+5.9
8	1	-4	12.4	+12.0
8	1	-3	13.6	+13.9
8	1	-2	7.8	+8.9
8	1	-1	18.3	+20.1
8	1	0	1.3	+1.7
8	1	1	14.9	-13.7
8	1	2	8.6	-8.5
8	1	3	12.2	-11.9
8	1	4	2.6	-2.7
8	1	5	3.5	+4.0
9	1	-12	1.1	+1.2
9	1	-11	1.5	-1.4
9	1	-10	5.3	-5.3
9	1	-9	5.9	+4.5
9	1	-8	7.4	+7.5
9	1	-7	6.1	-5.7
9	1	-6	6.8	-6.9
9	1	-5	3.4	-3.7
9	1	-4	1.3	-1.5
9	1	-3	1.7	+1.8
9	1	-2	5.1	+4.7
9	1	-1	9.7	+9.2
9	1	0	2.7	-2.5
9	1	1	8.6	-8.0
9	1	2	5.6	+5.2
9	1	3	6.1	+5.4
9	1	4	2.1	-2.4
10	1	-12	2.1	+1.9
10	1	-11	1.7	-1.6
10	1	-9	1.7	-1.1
10	1	-7	8.6	+8.2
10	1	-6	1.3	+1.3
10	1	-5	3.1	-3.4
10	1	-3	2.4	-2.9
10	1	-2	5.1	+4.7
10	1	-1	5.2	+5.6
10	1	0	2.9	-2.7
10	1	1	1.7	-1.8
10	1	2	4.2	-4.6
10	1	3	2.6	-2.7
11	1	-11	2.3	+1.9
11	1	-10	1.0	-1.0
11	1	-9	3.2	-2.9
11	1	-8	3.6	+3.4
11	1	-7	7.1	+6.4
11	1	-6	2.0	-2.3
11	1	-5	4.1	-4.3
11	1	-4	5.8	+5.3
11	1	-3	3.7	+3.3
11	1	-2	5.0	-5.1
11	1	-1	3.1	-3.1
11	1	0	0.7	+0.6
11	1	2	0.7	-0.6
12	1	-11	4.3	+3.9
12	1	-10	6.7	+6.4
12	1	-9	7.8	+7.6
12	1	-8	4.8	+5.9
12	1	-7	1.1	+1.2
12	1	-6	2.6	-2.8
12	1	-5	5.4	-5.8
12	1	-4	8.1	-8.5
12	1	-3	8.1	-8.7
12	1	-2	5.3	-5.1
12	1	-1	1.5	-1.3
12	1	0	1.7	+1.3
13	1	-9	2.1	-1.8
13	1	-8	2.4	+2.3
13	1	-7	2.3	+2.3
13	1	-6	1.7	+1.1
13	1	-5	1.9	+1.6
13	1	-4	2.1	+1.8
13	1	-3	2.6	-2.7
13	1	-2	3.7	-3.7
0	2	0	29.8	-30.3
0	2	1	23.3	-21.4
0	2	2	36.4	-36.9
0	2	3	1.3	+1.7
0	2	4	32.2	+32.5
0	2	5	1.5	+1.0
0	2	6	2.6	+1.7
0	2	7	18.6	+17.6
0	2	8	5.9	+4.7
0	2	9	2.1	-2.9
1	2	-10	2.7	+2.8
1	2	-9	4.8	+4.7
1	2	-8	10.3	-10.6
1	2	-7	8.8	-8.9
1	2	-6	2.4	+2.3
1	2	-5	6.5	+5.3
1	2	-4	27.9	+26.7
1	2	-3	5.1	+3.6
1	2	-2	13.8	-13.7
1	2	-1	11.1	+10.7
1	2	0	8.4	-8.9
1	2	1	13.6	+13.7
1	2	2	16.9	+16.5
1	2	3	32.9	-32.0
1	2	4	17.5	-13.5
1	2	5	4.4	-4.9
1	2	6	3.5	+2.9
1	2	7	14.5	+14.1
1	2	8	1.7	+1.3
1	2	9	3.2	-2.9
2	2	-10	3.4	+3.5
2	2	-9	1.0	-0.9
2	2	-7	0.9	-0.7
2	2	-6	5.9	-4.9
2	2	-5	2.2	-1.5
2	2	-4	8.5	-8.3
2	2	-3	0.5	-0.3
2	2	-2	12.2	+12.1
2	2	-1	14.7	-14.2
2	2	0	2.3	-2.3
2	2	1	7.5	+7.9
2	2	2	5.8	-5.5
2	2	3	9.7	+9.1
2	2	4	4.4	+3.9
2	2	5	4.8	-4.0
2	2	6	4.5	+4.0
2	2	7	1.3	+1.4
2	2	8	1.9	-0.7
2	2	9	0.8	+1.1
3	2	-11	1.6	+1.4
3	2	-10	3.1	+3.4
3	2	-9	2.9	+1.8
3	2	-8	1.8	+1.5
3	2	-7	5.5	+5.9
3	2	-6	0.9	-0.7
3	2	-5	1.9	-2.4
3	2	-4	2.2	-2.5
3	2	-3	20.6	-20.2
3	2	-2	16.0	-15.7
3	2	-1	6.2	-6.1
3	2	0	9.2	+8.5
3	2	1	21.7	+20.8
3	2	2	1.3	+1.3
3	2	3	1.7	-1.2
3	2	4	3.4	+3.3
3	2	5	1.3	-1.0
3	2	6	3.0	+2.5
3	2	7	1.7	+1.5
3	2	8	2.5	-2.6
3	2	9	1.6	-1.6
4	2	-11	3.7	+3.7
4	2	-10	3.7	+3.8
4	2	-9	5.9	-6.0
4	2	-8	9.2	-9.0
4	2	-7	4.3	-3.3
4	2	-6	12.2	-12.9
4	2	-5	28.8	-29.4
4	2	-4	5.8	-6.0
4	2	-3	19.1	+19.1
4	2	-2	9.9	+9.1
4	2	-1	9.9	+8.7
4	2	0	30.9	+29.9
4	2	1	25.8	+24.5
4	2	2	1.7	-1.2
4	2	3	3.3	-3.2
4	2	4	1.6	+1.2
4	2	5	5.1	-4.8
4	2	6	9.9	-10.9
4	2	7	3.2	-3.9
4	2	8	1.8	+1.9
5	2	-12	0.5	+0.7
5	2	-11	3.9	-3.8
5	2	-9	6.5	+7.0
5	2	-8	4.6	+4.4
5	2	-7	4.7	+3.8
5	2	-6	5.2	-4.9
5	2	-5	9.5	-9.4
5	2	-4	1.7	-1.0
5	2	-3	8.4	-8.1
5	2	-2	5.8	-6.1
5	2	0	7.1	-8.1
5	2	1	0.7	+0.5
5	2	2	11.8	+11.3
5	2	3	7.8	+7.8
5	2	4	4.5	+4.8
5	2	5	1.3	-1.5
5	2	6	2.4	-2.7
6	2	-12	2.3	-2.5
6	2	-11	3.1	-2.7
6	2	-9	1.8	-1.9
6	2	-8	1.8	+1.7
6	2	-7	2.5	+2.1
6	2	-6	1.7	-1.3
6	2	-5	3.5	+3.6
6	2	-4	2.4	-2.4
6	2	-3	1.7	-1.1
6	2	-2	8.2	+8.3
6	2	-1	1.5	-1.2
6	2	0	1.7	+1.7
6	2	1	2.1	+2.3
6	2	2	4.1	-3.7
6	2	3	1.3	+1.4
6	2	4	1.3	+0.8
6	2	5	3.0	-3.3
7	2	-12	4.0	-3.9
7	2	-11	5.8	-6.0
7	2	-10	3.4	+3.9
7	2	-9	0.8	-0.4
7	2	-8	1.3	-1.4
7	2	-7	1.3	-1.2
7	2	-6	13.6	-13.9
7	2	-5	2.4	+2.4
7	2	-4	16.6	+16.6
7	2	-3	11.7	+11.9
7	2	-2	11.8	+12.2
7	2	-1	11.0	-11.6
7	2	0	13.6	-13.8
7	2	1	5.0	+4.3
7	2	2	1.9	+0.8
7	2	3	2.1	+2.1
7	2	5	5.8	-6.0
7	2	6	0.5	-0.7
8	2	-12	6.5	-6.9
8	2	-11	2.6	-2.6
8	2	-10	2.4	+0.8
8	2	-9	2.4	+2.4
8	2	-8	3.7	+3.9
8	2	-7	9.3	+9.9
8	2	-6	20.3	+21.3
8	2	-5	4.1	+4.4
8	2	-4	6.7	-7.1
8	2	-3	9.6	+10.1
8	2	-2	2.6	-2.3
8	2	-1	20.3	-20.3
8	2	0	9.3	-9.1
8	2	1	4.6	-4.2
8	2	2	3.6	-3.9
8	2	3	1.7	-1.5
8	2	4	2.1	+2.2
8	2	5	5.7	+6.2
9	2	-12	4.6	-4.2
9	2	-10	2.5	+1.8
9	2	-8	2.1	+1.7
9	2	-7	10.5	-9.8
9	2	-6	9.3	-8.6
9	2	-5	10.2	+9.5
9	2	-4	10.2	+10.3
9	2	-3	10.2	+10.9
9	2	-2	0.9	+0.6
9	2	-1	9.4	-9.0
9	2	3	1.7	+1.4
9	2	4	5.7	-5.4
10	2	-11	1.2	-0.9
10	2	-10	1.0	-0.7
10	2	-9	4.3	+4.0
10	2	-6	2.1	+1.4
10	2	-5	3.2	-2.7
10	2	-2	2.2	-2.0
10	2	-1	0.5	+0.7
10	2	0	2.4	-1.9
10	2	1	2.6	-2.4
10	2	2	1.2	+1.0
11	2	-11	2.9	+2.2
11	2	-10	4.2	+3.8
11	2	-9	3.8	+3.7
11	2	-7	2.0	-1.9
11	2	-5	1.6	-1.2
11	2	-4	3.0	-2.6
11	2	-3	1.9	-1.5
11	2	-2	3.3	-3.2
11	2	-1	1.7	-1.6
11	2	0	1.5	+1.4
11	2	1	3.1	+2.7
12	2	-10	2.5	+2.0
12	2	-9	1.3	+0.9
12	2	-8	7.9	-7.9
12	2	-7	9.2	-8.8
12	2	-6	3.4	-2.7
12	2	-5	4.1	-3.9
12	2	-4	6.7	-6.7
12	2	-3	1.4	+1.2
12	2	-2	9.5	+8.7
12	2	-1	4.8	+4.9
13	2	-8	5.0	+5.3
13	2	-7	2.5	+2.5
13	2	-6	2.3	-1.9
13	2	-5	4.4	-4.1
13	2	-4	4.0	-4.1
13	2	-3	0.9	-0.6
0	3	1	3.2	+3.0
0	3	2	9.0	+9.7
0	3	3	10.2	+10.7
0	3	4	17.2	+17.6
0	3	5	12.8	+13.6
0	3	6	2.8	-2.3
0	3	7	7.1	-6.9
0	3	8	2.2	-1.7
0	3	9	1.5	-1.2
0	3	10	1.1	-1.1
1	3	-10	2.9	-2.9
1	3	-9	1.2	-1.9
1	3	-8	3.1	-2.9
1	3	-7	3.2	-2.7
1	3	-6	21.8	+20.7
1	3	-5	9.4	+3.7
1	3	-4	11.5	-11.1
1	3	-3	1.8	+1.2
1	3	-2	10.9	-10.2
1	3	-1	3.4	-3.2
1	3	0	0.7	+0.6
1	3	1	16.0	-15.3
1	3	2	1.6	-1.4
1	3	3	12.7	-13.1
1	3	4	5.9	-6.0
1	3	5	26.2	+27.0
1	3	6	9.9	+9.2
1	3	7	4.2	-4.0
1	3	8	0.8	+0.5
1	3	9	2.5	-2.9
2	3	-11	1.5	-1.2
2	3	-10	1.6	-1.4
2	3	-9	1.3	-1.1
2	3	-8	2.5	+2.0
2	3	-7	1.4	+1.2
2	3	-6	5.8	-5.4
2	3	-5	3.9	-2.6
2	3	-4	1.0	+1.0
2	3	-2	8.0	+7.7
2	3	-1	9.5	+9.1
2	3	0	2.4	-2.3
2	3	1	4.2	-3.8
2	3	2	0.8	+0.5
2	3	3	6.4	+6.0
2	3	4	4.4	+4.7
2	3	5	3.4	-3.4
2	3	6	3.6	-3.8
3	3	-11	1.5	+1.7
3	3	-10	2.4	-2.0
3	3	-9	2.4	+1.9
3	3	-7	7.8	-7.6
3	3	-6	9.2	-8.4
3	3	-5	4.1	-3.9
3	3	-4	1.7	-1.8
3	3	-3	13.2	-12.4
3	3	-2	2.7	+2.4
3	3	-1	31.3	+30.5
3	3	0	8.2	+8.2
3	3	1	3.7	-3.3
3	3	2	3.2	+3.1
3	3	3	3.1	-3.0
3	3	4	2.4	-2.3
3	3	5	1.4	-1.2
3	3	6	0.9	-0.7
3	3	8	4.0	-3.8
4	3	-11	2.0	-2.3
4	3	-10	1.9	-1.7
4	3	-9	3.8	-3.6
4	3	-8	5.8	-5.4
4	3	-7	3.5	-3.2
4	3	-6	5.1	+5.0
4	3	-5	8.5	+8.5
4	3	-4	8.6	+8.3
4	3	-3	16.0	+15.4
4	3	-2	12.6	+13.0
4	3	-1	2.0	+1.5

Table 2 (*cont.*)

H	K	L	F(OBS)	F(CAL)
4	3	0	3.1	-2.7
4	3	1	2.4	-2.4
4	3	2	5.8	-5.7
4	3	3	8.8	-8.4
4	3	4	7.8	-8.1
4	3	5	3.2	-2.9
4	3	8	1.7	+1.8
5	3	-11	1.7	+1.6
5	3	-10	0.7	+0.5
5	3	-9	5.7	+5.5
5	3	-8	2.9	-2.5
5	3	-7	12.4	-12.8
5	3	-6	2.8	-2.3
5	3	-5	1.0	-1.0
5	3	-4	3.8	-3.9
5	3	-2	3.6	+3.1
5	3	-1	9.2	+8.7
5	3	0	5.4	+5.6
5	3	1	5.0	+4.9
5	3	2	10.8	+11.2
5	3	3	2.0	-1.8
5	3	4	10.8	-10.4
5	3	5	2.4	-2.3
5	3	7	1.8	-2.0
6	3	-11	1.9	+1.8
6	3	-10	0.8	+0.8
6	3	-9	2.4	-2.3
6	3	-8	2.1	-1.5
6	3	-7	2.4	+2.8
6	3	-6	3.4	+3.3
6	3	-5	2.0	+2.0
6	3	-4	2.0	+2.1
6	3	-3	4.0	-3.7
6	3	-2	5.8	-5.6
6	3	-1	1.8	+1.8
6	3	0	3.2	+3.5
6	3	2	4.0	-3.8
6	3	3	3.1	-3.5
6	3	5	1.8	+1.6
7	3	-10	1.1	-0.7
7	3	-9	2.4	+2.0
7	3	-8	2.5	-2.1
7	3	-7	3.6	+3.6
7	3	-6	3.7	+3.6
7	3	-5	8.9	+7.6
7	3	-4	19.7	+19.7
7	3	-3	8.8	-9.0
7	3	-2	19.7	-20.3
7	3	0	2.4	-2.3
7	3	1	1.8	+1.5
7	3	2	4.0	+3.3
7	3	3	3.8	-3.4
7	3	5	0.9	-0.7
8	3	-11	3.1	+3.1
8	3	-10	3.2	+3.1
8	3	-9	2.5	+2.3
8	3	-8	3.4	+2.9
8	3	-7	2.5	+2.2
8	3	-6	2.9	+2.2
8	3	-5	2.5	-2.6
8	3	-4	14.3	-13.9
8	3	-3	14.3	-13.8
8	3	-2	2.2	-2.4
8	3	-1	1.4	+1.2
8	3	1	1.4	+1.3
8	3	2	1.3	+1.4
8	3	3	3.2	+3.0
8	3	4	3.5	+3.9
9	3	-10	2.5	+1.9
9	3	-9	3.0	-2.7
9	3	-8	1.8	-1.5
9	3	-7	3.1	+2.7
9	3	-6	2.0	+2.0
9	3	-5	14.6	+15.1
9	3	-4	6.5	+6.5
9	3	-3	13.0	-13.9
9	3	-2	5.5	-5.1
9	3	-1	2.2	-2.2
9	3	0	2.7	-2.6
9	3	1	1.6	+1.3
9	3	2	2.3	-2.1
9	3	3	0.9	-0.7
10	3	-10	1.5	-1.6
10	3	-9	1.6	-1.5
10	3	-7	1.8	+1.3
10	3	-5	4.7	-4.1
10	3	-4	3.8	-3.4
10	3	-3	1.9	+2.0
10	3	-2	1.8	+1.6
10	3	0	1.7	+1.4
10	3	1	1.0	-0.9
10	3	2	1.5	-1.0
11	3	-10	1.5	+1.2
11	3	-9	5.8	-5.4
11	3	-8	1.8	-1.6
11	3	-7	0.9	-0.8
11	3	-6	5.2	-5.0
11	3	-5	3.0	-2.7
11	3	-4	1.2	+1.0
11	3	-3	2.0	+1.5
11	3	-2	1.6	-1.0
11	3	-1	1.7	+1.5
11	3	0	6.4	+6.2
12	3	-8	2.5	-2.2
12	3	-7	2.5	-2.3
12	3	-6	0.6	+0.6
12	3	-5	3.8	+4.1
12	3	-4	5.2	+5.4
12	3	-3	3.2	+3.3
12	3	-2	3.2	+2.8
0	4	0	3.7	+3.7
0	4	1	3.0	+2.8
0	4	2	3.6	+3.3
0	4	3	13.0	+12.9
0	4	4	9.5	+8.5
0	4	5	13.4	-13.7
0	4	6	11.7	-11.8
0	4	7	1.2	+0.8
0	4	8	1.1	+1.6
1	4	-8	4.5	+5.4
1	4	-5	3.8	+3.5
1	4	-4	15.4	-15.2
1	4	-3	7.1	-7.1
1	4	-2	2.7	+3.2
1	4	-1	7.3	-7.9
1	4	0	1.6	+1.9
1	4	1	1.1	+1.4
1	4	2	3.1	+2.5
1	4	3	15.3	+15.7
1	4	4	2.9	+3.0
1	4	5	2.5	+2.4
1	4	6	4.0	+4.4
1	4	7	7.4	-7.8
1	4	8	3.2	-3.8
2	4	-10	2.4	+2.3
2	4	-9	1.6	+1.5
2	4	-8	1.2	-0.8
2	4	-7	0.8	-0.7
2	4	-6	4.0	-4.6
2	4	-5	1.2	-1.0
2	4	-4	6.7	+6.5
2	4	-3	7.7	+7.9
2	4	-2	4.0	+3.4
2	4	-1	7.3	-7.8
2	4	0	6.3	-6.1
2	4	1	1.8	+2.1
2	4	2	2.4	+3.0
2	4	3	3.4	+3.1
2	4	4	3.5	-2.6
2	4	5	6.5	-6.6
2	4	6	1.7	-1.1
2	4	7	2.2	+2.9
2	4	8	2.7	+2.9
3	4	-10	3.5	-3.4
3	4	-9	4.0	-4.4
3	4	-8	2.8	-2.8
3	4	-7	1.9	-1.4
3	4	-6	1.2	+1.1
3	4	-4	6.0	+6.0
3	4	-3	12.2	+13.1
3	4	-2	3.6	+3.7
3	4	-1	3.8	+4.0
3	4	0	3.2	+3.4
3	4	1	7.4	-8.2
3	4	2	7.3	-6.7
3	4	3	4.5	-4.1
3	4	5	2.2	+2.1
3	4	6	2.9	-2.4
3	4	7	1.0	-0.5
4	4	-10	2.7	+2.3
4	4	-9	1.9	-1.8
4	4	-8	1.0	+0.9
4	4	-7	8.3	+8.9
4	4	-6	4.4	+4.8
4	4	-5	1.2	-1.5
4	4	-4	1.1	+1.1
4	4	-3	3.1	+3.2
4	4	-2	5.4	-5.6
4	4	-1	11.2	-11.7
4	4	0	1.6	-1.4
4	4	1	1.1	+0.8
4	4	2	8.7	-8.5
4	4	3	4.4	-4.1
4	4	4	4.4	+4.0
4	4	5	1.8	+1.4
4	4	7	2.8	+2.7
5	4	-10	3.9	-2.9
5	4	-9	3.1	-3.6
5	4	-7	3.1	-3.9
5	4	-5	7.3	+7.5
5	4	-4	3.0	+2.6
5	4	-3	2.8	+3.3
5	4	-2	7.3	+7.2
5	4	-1	4.4	+5.0
5	4	0	0.7	+0.8
5	4	1	5.5	-6.3
5	4	2	7.1	-7.2
5	4	3	2.5	-2.4
5	4	4	4.2	-3.9
5	4	5	2.1	-1.8
5	4	6	2.2	+2.0
6	4	-10	1.2	-1.3
6	4	-9	1.4	-1.4
6	4	-8	2.4	+2.7
6	4	-7	4.4	+5.2
6	4	-6	1.8	+1.7
6	4	-5	3.6	-3.5
6	4	-4	7.8	-8.7
6	4	-3	1.2	-1.3
6	4	-2	4.5	+5.4
6	4	-1	1.3	+1.5
6	4	1	3.0	-3.5
6	4	2	3.6	-3.7
6	4	3	3.4	+3.2
6	4	4	3.4	+3.3
6	4	5	1.2	+0.9
7	4	-9	3.0	+3.3
7	4	-8	2.4	+2.5
7	4	-7	1.7	+1.3
7	4	-6	5.8	+6.2
7	4	-5	5.8	-6.6
7	4	-4	9.9	-10.0
7	4	-3	1.4	-1.3
7	4	-2	7.1	-7.3
7	4	-1	0.8	-0.5
7	4	0	5.1	+5.2
7	4	2	3.2	+3.0
8	4	-10	1.0	-1.1
8	4	-9	1.5	-1.4
8	4	-6	1.9	-1.6
8	4	-5	11.6	-11.2
8	4	-4	8.1	-8.7
8	4	-3	9.1	+9.4
8	4	-2	9.9	+9.8
8	4	0	1.6	-1.0
8	4	1	1.2	+0.7
8	4	2	2.4	+2.3
8	4	3	2.2	+2.2
9	4	-9	1.9	+2.5
9	4	-8	1.1	+1.3
9	4	-7	4.2	+4.3
9	4	-5	4.9	-5.3
9	4	-3	8.5	-8.3
9	4	-2	6.4	-6.2
9	4	-1	4.0	+4.6
9	4	0	1.5	+1.2
9	4	1	1.4	+1.3
9	4	2	2.0	+2.2
10	4	-9	2.0	+2.3
10	4	-8	1.9	+1.6
10	4	-7	2.1	-1.9
10	4	-6	1.8	-2.0
10	4	-5	1.6	-1.6
10	4	-4	0.8	+1.0
10	4	-3	3.9	+4.5
10	4	-2	3.1	+3.1
10	4	-1	1.4	-1.1
10	4	0	3.7	-3.4
11	4	-8	3.6	-3.6
11	4	-6	1.7	+2.0
11	4	-5	2.7	+2.9
11	4	-4	1.5	+1.4
11	4	-3	1.7	+1.3
11	4	-2	4.4	+3.7
0	5	1	7.0	+6.4
0	5	2	8.5	+7.6
0	5	3	9.2	-8.3
0	5	4	8.1	-7.6
0	5	6	3.5	-3.2
0	5	7	3.3	+3.2
0	5	8	2.4	+2.8
0	6	0	8.6	+8.9
0	6	1	2.2	-1.6
0	6	2	5.1	-4.8
0	6	4	2.9	-2.7
0	6	6	1.7	+1.3
0	7	1	2.8	+3.3
0	7	2	2.8	-2.5

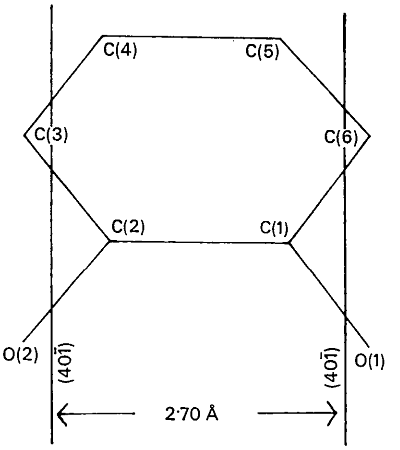

Fig. 1. Orientation of molecule to give maximum value of $F(40\bar{1})$.

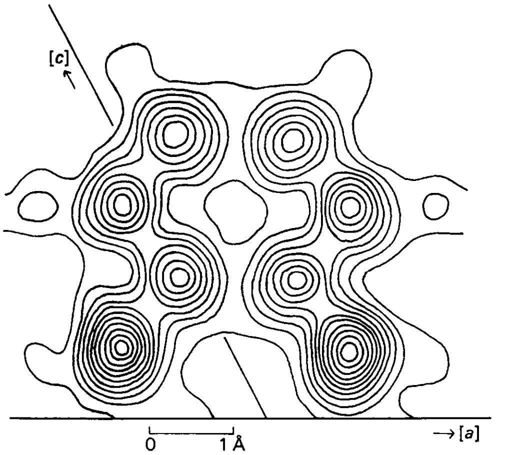

Fig. 2. Projection of electron density along **b**. The contours are approximately at intervals of 1 e.Å^{-2}, the outer contour being zero.

Determination of the structure

A survey of the $\{h0l\}$ structure amplitudes showed that $F(40\bar{1})$ was the largest, and as it was almost the maximum possible value for that plane which had a spacing of 2·70 Å it was thought that the molecular orientation would probably be as in Fig. 1. On this assumption, a set of x and z coordinates was prepared which was also reasonable from space filling considerations. Three cycles of $F(h0l)$ calculations and least-squares refinement of x and z on the computer, using a weighting scheme which rejected from the least-squares totals terms where $F(\text{calc}) < \frac{1}{3}F(\text{obs})$, reduced the residual R to 16%. An electron density map of the **b** projection at this stage is shown in Fig. 2.

The observation that $F(012)$ was the largest structure amplitude suggested that the molecule, which was expected to be planar, would lie in the (012) plane. This enabled the approximate y atomic coordinates to be deduced; a few preliminary structure factor calculations confirmed that the postulated molecular arrangement was correct. The first complete set of $\{hkl\}$ structure amplitude calculations gave $R=27\%$, and from this point refinement was continued on the computer.

Refinement of the structure

Seven cycles of structure amplitudes and least-squares calculations were carried out on our Ferranti Pegasus computer, with programs written by Cruickshank & Pilling (1961) as a result of which the residual R was reduced to 5·8%. The first cycle used all the $F(hkl)$ but rejected from the totals terms where the agreement was poor, *i.e.* where $F(\text{calc}) < \frac{1}{2}F(\text{obs})$. In the second cycle anisotropic temperature factors were calculated for the carbon and oxygen atoms and the normal weighting scheme ($w \propto 1/F$) was applied.

The hydrogen atoms were included at their calculated positions, assuming C–H and O–H to be 1·08 Å. The positions of the four hydrogen atoms attached to the carbon atoms of the benzene ring were unambiguous, but the two attached to the oxygen atoms could occupy either of a pair of positions depending on the sequence in the helical hydrogen-bond system. Obviously there is a possibility of disorder of the hydrogen atoms in the structure, depending on whether the direction of the hydrogen bonds is *up* or *down* the screw axis. A difference projection along **b** showed a small amount of positive electron density for both positions, but when a full $\{hkl\}$ cycle was computed with half-hydrogen atoms in each of the alternative positions the site occupation for one pair, as indicated by an increase in the isotropic temperature factors, was only about one-tenth of that for the other pair of positions. It was concluded that in the particular specimen used for this set of intensity data, the majority of the hydrogen bonds were in the same sense with respect to the screw axis direction, and the data were treated accordingly.

The positional and thermal atomic parameters obtained at the end of the refinement, which was judged to be complete when the mean shift indicated was less than half the mean standard deviation, are listed in Table 1. The final agreement between observed and calculated structure amplitudes is shown in Table 2. In addition to the 912 terms used in the refinement, there were a further 63 terms with zero or unobserved intensity; the calculated structure amplitudes for all these were found to be less than 1.

It is worth putting on record that the whole of this structure determination, from the selection of the specimen to the completion of the refinement, was carried out in 15 working days.

Description of the structure

Pairs of catechol molecules, related by a centre of symmetry, are linked together by means of two hydrogen bonds. Successive pairs of molcules form thick layers parallel to (001) by means of a further system of hydrogen bonds which form helices around the crystallographic screw axes. As there are only van der Waals forces between the layers, (001) is a strong cleavage plane. The possibility of left- or right-handed helices with respect to the hydrogen bond direction confers potential disorder on the structure, although in the specimen used in this investigation the majority of the hydrogen bond helices appeared to be in the same direction.

The bond lengths and inter-bond angles are listed in Table 3, and are also shown in Fig. 3 which is a diagram of the orientation of the molecule in the unit cell.

The benzene ring of the catechol molecule is approximately planar, its equation referred to standard orthogonal axes being

$$0{\cdot}0614X-0{\cdot}6847Y+0{\cdot}7260Z=-0{\cdot}2406\,.$$

The atoms are displaced from this plane by the following amounts: C(1) −0·001, C(2) −0·007, C(3)

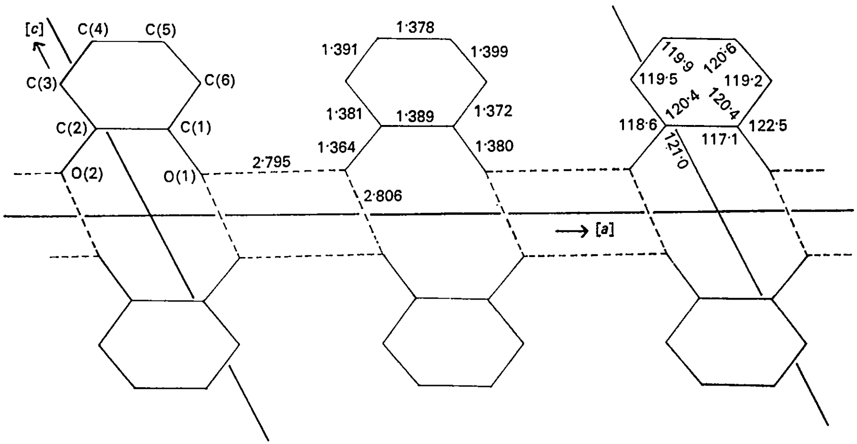

Fig. 3. Diagram of molecular orientation in the unit cell, showing the helical hydrogen bonding system in projection, and part of a layer of catechol molecules.

Table 3. *Bond lengths and inter-bond angles*

C(1)–C(2)	1·389 Å	C(1)–C(2)–C(3)	120·4°
C(2)–C(3)	1·381	C(2)–C(3)–C(4)	119·5
C(3)–C(4)	1·391	C(3)–C(4)–C(5)	119·9
C(4)–C(5)	1·378	C(4)–C(5)–C(6)	120·6
C(5)–C(6)	1·399	C(5)–C(6)–C(1)	119·2
C(6)–C(1)	1·372	C(6)–C(1)–C(2)	120·4
C(1)–O(1)	1·380	C(6)–C(1)–O(1)	122·5
C(2)–O(2)	1·364	C(2)–C(1)–O(1)	117·1
O(1)–H–O(2′)	2·795	C(1)–C(2)–O(2)	121·0
O(2)–H–O(1′)	2·806	C(3)–C(2)–O(2)	118·6

+0·007, C(4) −0·002, C(5) −0·003, C(6) +0·006 Å. The two oxygen atoms are −0·014 and −0·056 Å respectively out of this plane, this slight distortion from rigorous overall planarity probably being enforced by packing considerations.

The mean C–C bond length is 1·385 Å, and the mean C–O bond length 1·372 Å, which compare with the values of 1·39 and 1·36 Å respectively found in resorcinol (Robertson, 1936). The mean hydrogen bond length (2·801 Å) is however rather longer than the mean (2·70 Å) in the resorcinol structure.

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Short Communications

Contributions intended for publication under this heading should be expressly so marked; they should not exceed about 1000 *words; they should be forwarded in the usual way to the appropriate Co-editor; they will be published as speedily as possible. Publication will be quicker if the contributions are without illustrations.*

Acta Cryst. (1966). **21**, 174

The space group and unit cell of cyclohex-2-ene-1, 4-dione.

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With an interest in the conformation of cyclohex-2-ene-1,4-dione, $C_6H_6O_2$, prepared by Garbisch (1965), we started the crystal structure determination of this compound. Short needle-shaped crystals were enclosed in capillaries to prevent sublimation. From precession photographs (Mo $K\alpha$, $\lambda=0{\cdot}7107$ Å), the monoclinic cell dimensions were found to be

$$a=6{\cdot}92\pm0{\cdot}01\ \text{Å}$$
$$b=6{\cdot}82\pm0{\cdot}01$$
$$c=6{\cdot}07\pm0{\cdot}01$$
$$\beta=97°20'\pm10'$$

where a is the needle axis. From systematic extinctions ($0k0$, $k=2n+1$; $h0l$, $h+l=2n+1$) the space group was determined to be $P2_1/n$. By comparison with the molecular volumes of quinol (132 Å^3/molecule) and quinhydrone (2 × 126 Å^3/molecule), it was concluded that there are two molecules per unit cell, since this would give a molecular volume for cyclohex-2-ene-1,4-dione of 142.1 Å^3. Also, crystals sink very slowly in glycerin, which suggests that the density is slightly greater than 1·28 g.cm^{-3}, the value for glycerin. For $Z=2$, the calculated density is 1·285 g.cm^{-3}.

With two molecules per unit cell, for space group $P2_1/n$, the molecule must lie on a center of symmetry. Since no reasonable structure for cyclohex-2-ene-1,4-dione contains a center of symmetry, the structure must be disordered. Therefore, we plan no further work on this compound.

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