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The Crystal Structure of 5,5-Dihydroxybarbituric Acid Trihydrate

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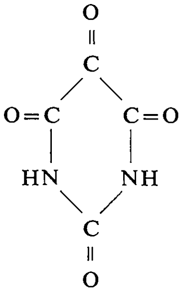
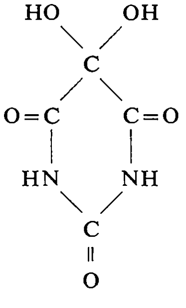
The crystal structure of 5,5-dihydroxybarbituric acid trihydrate, usually misnamed alloxan tetrahydrate, has been determined by a three-dimensional analysis with the use of photographic data. The space group is $C2/m$ with $a=9\cdot579\pm0\cdot005$, $b=12\cdot267\pm0\cdot007$, $c=7\cdot400\pm0\cdot010$ Å, $\beta=90\cdot75\pm0\cdot25°$, and $V=869\cdot5$ Å^3. There are four formula units $C_4H_4O_5N_2 . 3H_2O$ in the unit cell. The organic molecules are in special positions with the pyrimidine rings perpendicular to the crystallographic mirror planes. The twelve water molecules in the unit cell occupy a general eightfold position and a fourfold position of point symmetry 2. Hydrogen bonding links the organic molecules into straight ribbons extending infinitely along the twofold axis. The water molecules hydrogen-bond these ribbons into buckled sheets parallel to (201). There is no hydrogen bonding between these sheets. Three of the six hydrogen atoms of the asymmetric unit could be located by means of a difference Fourier synthesis. The remaining three were not observed on the difference maps and must, in fact, be disordered to fit into the hydrogen-bonding scheme and the symmetry of the crystal structure.

Introduction

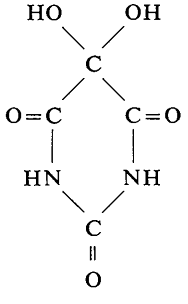
Oxidation of uric acid with nitric acid yields $C_4H_2O_4N_2$, a derivative of barbituric acid with the trivial name *alloxan*. Three crystalline phases of this compound are known (Beilstein, 1936), usually called anhydrous alloxan, alloxan monohydrate and alloxan tetrahydrate. Anhydrous alloxan, or 5-oxobarbituric acid (2,4,5,6-tetraoxoperhydropyrimidine) (I) was shown by Bolton (1964) to form no hydrogen bonds in the crystalline state, although it possesses the necessary NH and CO groups. The monohydrate was found by Singh (1960) to be composed of a different molecule, that of 5,5-dihydroxybarbituric acid or 2,4,6-trioxo-5,5-dihydroxyperhydropyrimidine (II) and to contain no water of crystallization. On the other hand the molecule (II) is sometimes referred to as alloxan itself (Fieser & Fieser, 1956), and for the discussion of reactions in aqueous solution, the distinction is generally not relevant. It seemed likely, therefore, that alloxan tetrahydrate was also misnamed. This structure analysis shows that this is indeed so; alloxan tetrahydrate is really 5,5-dihydroxybarbituric acid trihydrate (III). The details of the molecular structure and of the hydrogen-bonding in the crystal have been determined by three-dimensional single-crystal structure analysis.



(I)



(II)



$+3H_2O$

(III)

Crystal data

5,5-Dihydroxybarbituric acid trihydrate crystallizes together with the anhydrous compound when aqueous solutions of alloxan evaporate at room temperature. Platy crystals several millimeters in diameter are easily obtained. On exposure to the air they form powder pseudomorphs by losing water and transforming to the anhydrous compound.

The crystals are monoclinic with morphological symmetry $2/m$. The cell dimensions are

$$a=9\cdot579\pm0\cdot005 \text{ Å}$$
$$b=12\cdot267\pm0\cdot007$$
$$c=7\cdot400\pm0\cdot010$$
$$\beta=90\cdot75\pm0\cdot25°$$
$$V=869\cdot5 \text{ Å}^3$$

measured with Cu $K\alpha_1$ (1·5405 Å) and Cu $K\alpha_2$ (1·5443 Å) radiation. The observed density was $D_m=1\cdot639\pm0\cdot009$ g.cm^{-3} by flotation in a mixture of carbon tetrachloride and methylene iodide. With four formula units of $C_4H_4O_5N_2 . 3H_2O$, $M=214\cdot1$, in the unit cell the calculated density is $D_x=1\cdot635$ g.cm^{-3}, $F(000)=448$.

The systematic absences (hkl) for $h+k$ odd indicate a C-centered lattice and a choice of the space groups $C2$, Cm and $C2/m$, none of which could be eliminated by considerations of molecular symmetry. A statistical

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test of the distribution of the intensities and certain features of the Patterson function described below established $C2/m$.

Experimental

The crystals were enclosed in thin-walled capillaries. They decomposed on X-ray exposure so that several different crystals had to be used for the data collection. The dimensions of the rectilinear-shaped crystals used were always less than 0·4 mm. Three-dimensional intensity data were recorded in the usual way on multiple-film Weissenberg photographs using integration and equi-inclination techniques with Cu $K\alpha$ radiation, for which the linear absorption coefficient is $\mu = 14{\cdot}6$ cm^{-1}. Layers $0kl$ to $7kl$ were recorded about the a axis, $h0l$ to $h4l$ about b, and $hk0$ to $hk3$ about c. The intensities were estimated visually using a calibrated intensity standard and the data were reduced to structure amplitudes by means of a series of IBM 7070 programs written by McMullan (1964). In these programs, weights are assigned to the intensities according to the estimated reliability and frequency of their estimation and these weights are used in the calculations of film factors and average intensities. These weights are again used in the calculation of interlayer scale factors, by the method of Rollett & Sparks (1960), and in the final averaging for reflexions occurring on more than one layer. No corrections for absorption and extinction were applied. Of the 994 possible independent reflexions within the Cu $K\alpha$ sphere, 982 were recorded. Of these, 108 were too weak to be estimated and were assigned half the minimum observed intensity.

The structure analysis and refinement

Preliminary values for the scale factor and a uniform isotropic temperature factor were obtained from a Wilson plot and were used to compute the normalized structure amplitudes. The mean value of the normalized structure amplitudes was 0·818 as compared with the theoretical value of 0·798 for centric and 0·886 for non-centric structures (Wilson, 1949). This and the distribution curve of these values indicated that the structure is centrosymmetric. An inspection of the sharpened three-dimensional Patterson synthesis computed by the program of Chu & McMullan (1962), revealed a well-occupied Harker plane ($v=0$) and a recognizable Harker line ($u=0$, $w=0$). The space group was therefore most likely $C2/m$, and this was confirmed by the subsequent complete structure determination.

With four molecules in the unit cell, the molecular symmetry must be 2 or m. The distribution of vector peaks in the Patterson synthesis showed that there was an atomic concentration on or midway between the (202) planes and that one ring diagonal was perpendicular to the b axis. This eliminated the (h) and (g) positions which require twofold axial molecular symmetry and placed the center and the atoms C(2) and C(5) of the molecule at (i), $(0, 0, 0; \frac{1}{2}, \frac{1}{2}, 0) + x, 0, z; \bar{x}, 0, \bar{z}$ (see Fig. 1).

Based on this interpretation, coordinates for the pyrimidine ring atoms were deduced from the Patterson synthesis. With initial phases calculated from these atoms only, the ring substituents and water molecules could be located by a stepwise procedure of several cycles of Fourier syntheses and subsequent structure factor calculations. The agreement index for the first complete trial structure was 0·29. Successive refinement by three-dimensional differential Fourier synthesis with the use of isotropic and then anisotropic temperature factors on an IBM 7070 program (Shiono,

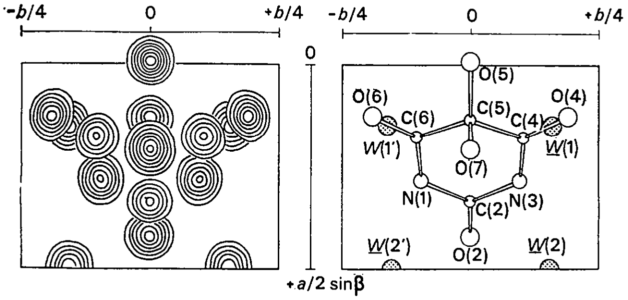


Fig. 1. Composite electron density map of 5,5-dihydroxybarbituric acid trihydrate viewed in the c-axis direction. Contour interval is 2 e.Å^{-3}, with zero omitted. Complementary drawing shows the molecule and numbering of atoms.

Table 1. *Fractional atomic coordinates and thermal parameters*

Estimated standard deviations in parentheses refer to the last decimal position reported. The expression for the temperature factor exponent consistent with the β-values is $-(\beta_{11}h^2+\beta_{22}k^2+\beta_{33}l^2+2\beta_{12}hk+2\beta_{13}hl+2\beta_{23}kl)$.

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
C(2)	0·3371(5)	0	−0·0889(6)	0·0048(4)	0·0025(3)	0·0073(6)	0	0·0012(4)	0
C(4)	0·1821(3)	0·1042(2)	0·1042(4)	0·0048(3)	0·0021(2)	0·0068(5)	0·0000(2)	0·0009(3)	−0·0001(2)
C(5)	0·1374(4)	0	0·2002(5)	0·0043(4)	0·0022(2)	0·0067(6)	0	0·0015(4)	0
N(3)	0·2862(3)	0·0961(2)	−0·0205(3)	0·0051(3)	0·0021(2)	0·0083(5)	0·0000(2)	0·0017(3)	0·0007(2)
O(2)	0·4228(4)	0	−0·2074(5)	0·0066(4)	0·0037(2)	0·0135(7)	0	0·0057(4)	0
O(4)	0·1295(3)	0·1916(2)	0·1437(4)	0·0091(3)	0·0021(2)	0·0140(5)	0·0008(2)	0·0049(3)	−0·0004(2)
O(5)	−0·0064(3)	0	0·2162(4)	0·0046(3)	0·0024(2)	0·0119(6)	0	0·0028(5)	0
O(7)	0·2118(4)	0	0 3654(4)	0·0090(4)	0·0033(2)	0·0059(5)	0	−0·0009(4)	0
W(1)	0·1534(3)	0·1611(2)	−0·3883(4)	0·0084(3)	0·0042(2)	0·0167(6)	−0·0007(2)	−0·0010(3)	0·0003(3)
W(2)	0·5	0·1534(3)	−0·5	0·0128(6)	0·0029(2)	0·0189(8)	0	0·0076(6)	0
H(N3)	0·309	0·153	−0·081						
H(1*W*1)	0·133	0·218	−0·481						
H(*W*2)	0·475	0·107	−0·405						

Table 2. *The observed and calculated structure factors*

The five columns between vertical lines are h, k, l, $|F_o|$ and F_c. The 108 unobserved and 16 strong low order reflexions which were omitted from the least-squares refinement are marked with an asterisk.

2	0	0	41.4*	-57.0
4	0	0	28.3	-28.5
6	0	0	47.7	57.0
8	0	0	8.9	8.5
10	0	0	5.4	5.2
12	0	0	1.1*	1.3
1	1	0	27.6	28.4
3	1	0	36.5	-45.9
5	1	0	14.3	13.2
7	1	0	28.5	34.4
9	1	0	1.7*	0.6
11	1	0	2.0	1.5
0	2	0	48.0*	73.3
2	2	0	11.8	-9.2
4	2	0	39.3	45.4
6	2	0	4.9	-2.2
8	2	0	13.9	-12.7
10	2	0	8.8	9.5
12	2	0	5.2	5.0
1	3	0	25.3	-25.6
3	3	0	64.2*	97.5
5	3	0	47.5	55.4
7	3	0	11.6	-10.7
9	3	0	24.0	26.8
11	3	0	1.2*	0.5
0	4	0	6.7	-0.9
2	4	0	35.3	37.8
4	4	0	9.0	-9.2
6	4	0	14.3	-14.2
8	4	0	11.9	11.6
10	4	0	3.8	-3.2
1	5	0	37.1	43.9
3	5	0	25.8	-26.7
5	5	0	15.8	15.8
7	5	0	15.1	15.1
9	5	0	26.2	31.0
11	5	0	15.4	-19.5
0	6	0	77.3*	102.9
2	6	0	34.3	35.9
4	6	0	28.5	-28.6
6	6	0	25.3	24.6
8	6	0	19.7	22.0
10	6	0	8.6	-9.2
1	7	0	6.8	-6.3
3	7	0	14.1	-12.3
5	7	0	23.8	24.1
7	7	0	2.1*	0.5
9	7	0	9.5	9.8
0	8	0	34.2	35.5
2	8	0	3.4	1.2
4	8	0	24.8	25.5
6	8	0	9.5	8.8
8	8	0	10.3	-10.4
10	8	0	6.2	6.3
1	9	0	3.8	3.1
3	9	0	19.8	19.7
5	9	0	20.8	20.8
7	9	0	7.3	7.5
9	9	0	7.0	7.0
0	10	0	50.6	61.5
2	10	0	22.0	-21.7
4	10	0	4.6	-5.1
6	10	0	4.0	3.9
8	10	0	1.0*	-2.8
1	11	0	16.6	16.7
3	11	0	3.2	-3.3
5	11	0	2.9	2.2
7	11	0	18.5	20.3
0	12	0	38.7	43.5
2	12	0	5.9	-3.5
4	12	0	4.4	3.6
6	12	0	10.9	10.6
1	13	0	8.5	-8.2
3	13	0	6.5	5.3
5	13	0	6.9	6.2
0	14	0	6.8	6.2
2	14	0	12.3	12.7
4	14	0	3.1	3.8
1	15	0	5.1	4.7
3	15	0	5.0	4.3
0	0	1	35.7*	61.7
2	0	1	61.3*	-145.9
-2	0	1	19.9	22.2
4	0	1	4.0	0.1
-4	0	1	29.4	-29.4
6	0	1	7.0	-7.3
-6	0	1	9.7	-9.7
8	0	1	2.8*	1.7
-8	0	1	20.9	-22.1
10	0	1	7.5	7.7
-10	0	1	5.8	5.9
12	0	1	2.6	-2.7
-12	0	1	7.8	-7.3
1	1	1	16.2	-13.9
-1	1	1	21.7	24.6
3	1	1	49.1*	76.1
-3	1	1	24.4	24.3
5	1	1	2.0	1.0
-5	1	1	31.8	-29.5
7	1	1	21.8	23.4
-7	1	1	20.1	18.7
9	1	1	3.8	-3.7
-9	1	1	1.9*	1.0
11	1	1	1.6*	1.9
-11	1	1	12.8	14.6
0	2	1	35.0	47.7
2	2	1	31.8	-37.5
-2	2	1	36.5	42.2
4	2	1	18.3	15.4
-4	2	1	10.8	-10.1
6	2	1	6.9	6.1
-6	2	1	25.5	28.9
8	2	1	2.0*	-0.5
-8	2	1	9.9	-9.0
10	2	1	5.7	5.1
-10	2	1	10.9	-10.6
12	2	1	10.4	10.8
-12	2	1	1.0*	0.2
1	3	1	32.8	-37.7
-1	3	1	21.0	-24.0
3	3	1	23.7	23.4
-3	3	1	43.9	-51.1
5	3	1	6.6	5.5
-5	3	1	18.2	-17.0
7	3	1	1.8*	-0.6
-7	3	1	6.0	5.6
9	3	1	8.9	-8.4
-9	3	1	4.8	0.9
11	3	1	3.2	-3.5
-11	3	1	5.5	-5.2
0	4	1	6.7	2.4
2	4	1	13.3	15.4
-2	4	1	67.8*	105.8
4	4	1	20.5	-18.9
-4	4	1	22.4	-20.4
6	4	1	24.7	26.1
-6	4	1	8.3	5.6
8	4	1	14.0	14.2
-8	4	1	14.5	14.8
10	4	1	11.8	-11.9
-10	4	1	11.8	-12.2
1	5	1	12.7	-12.2
-1	5	1	17.7	14.5
3	5	1	15.5	1.59
-3	5	1	4.3	2.9
5	5	1	5.8	5.0
-5	5	1	17.5	-18.4
7	5	1	15.4	14.4
-7	5	1	17.9	-18.0
-9	5	1	28.5	33.3
-11	5	1	4.9	-4.8
0	6	1	47.1	-49.7
2	6	1	13.1	12.2
-2	6	1	47.5	52.0
4	6	1	34.7	-34.3
-4	6	1	15.6	-12.9
6	6	1	4.9	-3.9
-6	6	1	19.1	-20.0
8	6	1	15.8	16.7
-8	6	1	1.7*	-1.8
-10	6	1	5.1	-4.8
1	7	1	10.8	8.6
-1	7	1	19.0	-17.6
3	7	1	54.9	58.3
-3	7	1	14.2	11.7
5	7	1	3.7	0.9
-5	7	1	18.4	16.2
7	7	1	2.3*	0.8
-7	7	1	8.9	-7.4
9	7	1	11.0	11.2
-9	7	1	10.7	11.3
0	8	1	3.6	2.1
2	8	1	12.7	-12.0
-2	8	1	11.0	9.4
4	8	1	9.5	7.9
-4	8	1	5.8	-6.2
6	8	1	1.8*	-0.9
-6	8	1	19.6	18.4
8	8	1	5.9	-4.6
-8	8	1	10.4	-10.6
-10	8	1	10.2	-10.1
1	9	1	20.6	-19.8
-1	9	1	15.4	14.9
3	9	1	3.5	2.7
-3	9	1	21.2	-21.2
5	9	1	11.8	10.2
-5	9	1	21.2	-22.2
7	9	1	6.7	6.5
-7	9	1	17.0	17.2
-9	9	1	8.8	-7.9
0	10	1	49.0	55.0
2	10	1	45.7	-49.2
-2	10	1	29.7	31.3
4	10	1	10.7	9.5
-4	10	1	20.7	-21.2
6	10	1	22.5	22.8
-6	10	1	13.1	12.5
8	10	1	3.0	-3.0
-8	10	1	3.7	3.0
1	11	1	13.7	-12.2
-1	11	1	13.7	11.3
3	11	1	4.9	4.9
-3	11	1	1.8*	0.1
5	11	1	1.8*	-1.1
-5	11	1	23.4	-24.7
7	11	1	13.5	13.7
-7	11	1	9.5	9.1
0	12	1	2.8*	-1.5
2	12	1	8.7	-7.1
-2	12	1	1.8*	1.7
4	12	1	3.8	2.7
-4	12	1	4.9	3.3
6	12	1	7.4	-6.3
-6	12	1	1.4*	-0.1
1	13	1	5.6	4.4
-1	13	1	18.9	-17.9
3	13	1	28.6	33.1
-3	13	1	14.1	13.4
5	13	1	9.0	-6.5
-5	13	1	8.7	7.4
0	14	1	13.3	-12.7
2	14	1	7.2	5.9
-2	14	1	11.8	11.0
4	14	1	8.9	-7.4
-4	14	1	3.1	-3.4
1	15	1	4.0	-3.7
-1	15	1	8.0	7.5
3	15	1	3.8	-3.3
-3	15	1	2.8	-2.7
0	0	2	23.8	27.7
2	0	2	85.7*	-180.2
-2	0	2	61.0*	85.2
4	0	2	52.2	66.6
-4	0	2	14.9	-14.6
6	0	2	36.4	37.6
-6	0	2	22.8	-19.9
8	0	2	32.5	-32.5
-8	0	2	14.0	12.3
10	0	2	11.5	10.4
-10	0	2	2.0*	-1.7
-12	0	2	8.2	-8.7
1	1	2	38.5	-46.9
-1	1	2	27.2	-26.8
3	1	2	26.2	-21.2
-3	1	2	23.7	20.9
5	1	2	1.9	-2.2
-5	1	2	62.4*	-80.6
7	1	2	15.3	-14.7
-7	1	2	13.4	-11.9
9	1	2	20.6	-22.0
-9	1	2	10.5	-10.3
11	1	2	6.4	6.9
-11	1	2	3.3	4.2
0	2	2	35.7	-43.1
2	2	2	21.2	-20.9
-2	2	2	61.8*	-72.6
4	2	2	21.7	-19.3
-4	2	2	7.8	6.7
6	2	2	11.5	-10.0
-6	2	2	5.8	3.8
8	2	2	11.5	-9.5
-8	2	2	8.3	-7.8
10	2	2	8.3	8.0
-10	2	2	14.6	-16.0
1	3	2	67.2*	103.2
-1	3	2	57.2*	-88.4
3	3	2	31.7	32.3
-3	3	2	12.3	-9.1
5	3	2	40.2	-41.6
-5	3	2	25.4	25.8
7	3	2	7.4	-7.1
-7	3	2	26.5	-25.8
9	3	2	5.9	5.5
-9	3	2	2.9	-2.3
11	3	2	4.1	-4.2
-11	3	2	3.3	4.4
0	4	2	66.7*	-91.6
2	4	2	11.2	7.8
-2	4	2	30.0	-31.8
4	4	2	48.0	-57.6
-4	4	2	15.2	14.1
6	4	2	11.0	10.7
-6	4	2	28.1	-28.3
8	4	2	7.6	-6.5
-8	4	2	3.0	-3.0
10	4	2	8.1	-8.7
-10	4	2	9.5	-10.0
1	5	2	9.0	-7.1
-1	5	2	16.9	-16.3
3	5	2	30.7	-32.4
-3	5	2	17.4	16.4
5	5	2	14.7	14.8
-5	5	2	24.8	-23.8
7	5	2	9.1	-8.8
-7	5	2	48.4	-56.1
9	5	2	12.3	-13.8
-9	5	2	20.5	22.6
11	5	2	5.5	-5.8
-11	5	2	1.0*	-0.3
0	6	2	42.8	-44.1
2	6	2	27.4	-28.6
-2	6	2	48.2	51.4
4	6	2	10.6	-10.0
-4	6	2	11.4	3.8
6	6	2	34.0	36.9
-6	6	2	23.8	-25.0
8	6	2	16.3	-17.7
-8	6	2	16.5	17.0
10	6	2	5.1	-6.5
-10	6	2	6.8	-6.6
1	7	2	3.2	-0.3
-1	7	2	28.1	-31.6
3	7	2	16.1	-15.4
-3	7	2	20.4	-20.1
5	7	2	7.6	-6.7
-5	7	2	20.9	-21.0
7	7	2	18.9	-19.2
-7	7	2	22.4	-24.0
9	7	2	6.3	-7.0
-9	7	2	1.4*	-0.4
0	8	2	13.2	-12.7
2	8	2	6.1	-5.0
-2	8	2	25.4	-26.8
4	8	2	6.4	-5.4
-4	8	2	4.0	-3.0
6	8	2	5.7	-5.0
-6	8	2	11.3	9.6
8	8	2	8.4	-8.7
-8	8	2	1.5*	-0.4
10	8	2	8.0	9.1
-10	8	2	15.8	-15.7
1	9	2	16.6	15.8
-1	9	2	1.97	-20.3
3	9	2	12.8	12.3
-3	9	2	6.5	5.7
5	9	2	15.0	-13.8
-5	9	2	10.7	-10.3
7	9	2	6.6	-6.5
-7	9	2	3.4	-2.7
9	9	2	1.8	-1.7
-9	9	2	11.9	-10.7
0	10	2	14.1	-13.5
2	10	2	41.7	-47.4
-2	10	2	11.2	-8.7
4	10	2	7.9	7.2
-4	10	2	2.3*	-3.2
6	10	2	1.7*	0.0
-6	10	2	14.5	-14.0
8	10	2	11.2	-13.0
-8	10	2	9.4	-9.6
1	11	2	10.0	-9.9
-1	11	2	6.3	-4.8
3	11	2	1.8*	-0.9
-3	11	2	19.3	20.3
5	11	2	1.7*	1.2
-5	11	2	23.9	-26.2
7	11	2	1.8*	-0.5
-7	11	2	6.9	-7.3
0	12	2	2.3	-1.7
2	12	2	19.7	-20.8
-2	12	2	1.7*	-0.2
4	12	2	6.2	5.7
-4	12	2	2.1*	0.2
6	12	2	6.3	5.8
-6	12	2	4.5	-3.3
1	13	2	7.1	6.9
-1	13	2	20.1	-23.0
3	13	2	3.5	-3.4
-3	13	2	6.9	-7.2
5	13	2	12.8	-11.6
-5	13	2	10.2	-9.6
0	14	2	12.3	-12.6
2	14	2	6.9	7.1
-2	14	2	3.2	-3.1
4	14	2	10.6	-10.3
-4	14	2	6.0	5.2
1	15	2	5.7	5.2
-1	15	2	11.3	-11.8
0	0	3	31.9	-37.2
2	0	3	56.7*	-75.4
-2	0	3	55.9	-61.1
4	0	3	46.8	53.2
-4	0	3	7.5	-4.2
6	0	3	34.3	-33.6
-6	0	3	6.2	6.1
8	0	3	8.0	-7.1
-8	0	3	21.8	-23.5
10	0	3	2.2*	2.3
-10	0	3	3.7	3.2
1	1	3	3.4	-0.5
-1	1	3	4.9	-6.8
3	1	3	14.4	12.1
-3	1	3	28.7	22.7
5	1	3	25.6	-26.0
-5	1	3	9.9	9.7
7	1	3	8.1	-6.8
-7	1	3	8.2	-6.9
9	1	3	3.4	3.5
-9	1	3	18.7	-21.5
11	1	3	3.2	-2.7
-11	1	3	10.1	9.8
0	2	3	12.0	13.9
2	2	3	34.0	-35.8
-2	2	3	24.5	-23.8
4	2	3	33.3	32.7
-4	2	3	26.4	-27.2
6	2	3	18.5	-17.5
-6	2	3	13.4	12.2
8	2	3	5.5	-5.3
-8	2	3	12.1	12.3
10	2	3	6.6	5.9
-10	2	3	1.9*	1.7
1	3	3	20.8	-16.7
-1	3	3	11.3	9.1
3	3	3	29.8	-29.1
-3	3	3	36.5	-36.0
5	3	3	19.3	-19.6
-5	3	3	5.6	-5.0
7	3	3	23.3	-23.2
-7	3	3	23.6	-23.7
9	3	3	4.6	4.1
-9	3	3	3.1	-3.2
11	3	3	1.8	-1.5
-11	3	3	4.9	-4.4
0	4	3	29.0	-30.9
2	4	3	2.0	1.1
-2	4	3	2.5	-1.7
4	4	3	20.8	18.6
-4	4	3	6.7	7.6
6	4	3	7.1	6.1
-6	4	2	2.4	-3.2
8	4	3	13.7	-14.2
-8	4	3	7.2	7.3
10	4	3	1.7*	-0.3
-10	4	3	6.5	7.5
1	5	3	1.8*	-2.1
-1	5	3	11.8	-10.7
3	5	3	15.6	-15.0
-3	5	3	7.8	-5.0
5	5	3	2.0*	0.3
-5	5	3	50.1	52.4
7	5	3	15.7	-16.2
-7	5	3	46.6	-53.5
9	5	3	2.1*	1.0
-9	5	3	2.1*	-2.0
-11	5	3	11.4	11.9
0	6	3	38.7	-38.0
2	6	3	3.6	2.0
-2	6	3	38.9	-42.6
4	6	3	15.2	-13.8
-4	6	3	2.4*	0.8
6	6	3	3.2	1.1
-6	6	3	2.1*	-0.7
8	6	3	6.2	-7.2
-8	6	3	13.3	-13.0
10	6	3	7.5	-7.9
1	7	3	32.7	32.2
-1	7	3	9.2	9.8
3	7	3	12.5	-11.1
-3	7	3	21.8	-22.3
5	7	3	17.7	-17.7
-5	7	3	32.5	33.9
7	7	3	2.7*	-3.3
-7	7	3	14.5	-12.9
9	7	3	9.2	9.2
-9	7	3	5.2	-6.4
0	8	3	4.0	3.2
2	8	3	15.6	-16.3
-2	8	3	18.0	-16.5
4	8	3	11.8	11.5
-4	8	3	25.4	-24.4
6	8	3	15.0	-14.9
-6	8	3	8.2	7.8
8	8	3	2.0*	-2.8
-8	8	3	9.7	9.7
1	9	3	25.9	-27.6
-1	9	3	2.4*	1.5
3	9	3	3.6	4.1
-3	9	3	3.4	4.8
5	9	3	10.7	-10.4
-5	9	3	18.6	-18.0
7	9	3	15.6	-17.4
-7	9	3	3.3	-4.0
9	9	3	2.7	3.1
-9	9	3	11.6	-10.7
0	10	3	10.8	-10.4
2	10	3	27.6	-30.3
-2	10	3	10.4	11.8
4	10	3	42.9	48.1

Table 2 (*cont.*)

-4	10	3	5.9	4.9
6	10	3	13.8	-14.4
-6	10	3	1.9*	-0.4
8	10	3	10.8	-10.5
-8	10	3	1.5*	0.9
1	11	3	14.9	-14.5
-1	11	3	10.5	-10.5
3	11	3	5.0	5.0
-3	11	3	12.3	12.4
5	11	3	9.3	-9.8
-5	11	3	3.2	-3.1
7	11	3	6.8	-7.0
-7	11	3	8.1	-8.0
0	12	3	3.5	3.1
2	12	3	10.1	-10.3
-2	12	3	23.0	-23.3
4	12	3	3.5	3.7
-4	12	3	5.1	-5.9
6	12	3	10.0	-9.5
-6	12	3	8.3	7.3
1	13	3	21.7	24.1
-1	13	3	2.0*	-1.9
3	13	3	7.2	-6.9
-3	13	3	11.8	-11.0
5	13	3	15.2	-14.3
-5	13	3	17.4	16.8
0	14	3	5.0	-5.9
2	14	3	1.3*	0.7
-2	14	3	13.9	-12.7
4	14	3	5.5	-5.9
-4	14	3	2.8	-3.1
0	0	4	34.8	-36.6
2	0	4	38.2	37.6
-2	0	4	37.7	41.0
4	0	4	61.1	73.3
-4	0	4	24.5	22.2
6	0	4	35.2	-36.8
-6	0	4	6.3	4.9
8	0	4	5.6	4.4
-8	0	4	8.7	8.4
10	0	4	11.5	11.6
-10	0	4	10.4	10.9
1	1	4	19.4	-17.0
-1	1	4	32.4	-31.5
3	1	4	32.2	31.9
-3	1	4	45.6	49.3
5	1	4	27.1	-27.5
-5	1	4	2.9	-2.7
7	1	4	12.5	11.3
-7	1	4	21.3	21.4
9	1	4	3.9	3.5
-9	1	4	13.4	-14.7
11	1	4	2.5	1.6
-11	1	4	1.0*	-0.5
0	2	4	25.9	24.3
2	2	4	18.7	15.6
-2	2	4	12.9	12.6
4	2	4	4.9	-2.7
-4	2	4	33.0	-36.4
6	2	4	5.0	-4.3
-6	2	4	6.3	4.9
8	2	4	10.8	9.3
-8	2	4	15.5	16.4
10	2	4	2.7	-2.6
-10	2	4	3.7	2.9
1	3	4	42.6	46.2
-1	3	4	39.4	44.3
3	3	4	25.2	-25.8
-3	3	4	13.7	-12.1
5	3	4	13.7	-11.8
-5	3	4	29.5	29.6
7	3	4	32.0	33.6
-7	3	4	27.5	28.6
9	3	4	1.6*	0.9
-9	3	4	2.8	-3.6
0	4	4	2.4*	1.7
2	4	4	33.5	35.3
-2	4	4	6.2	-6.4
4	4	4	24.4	-22.3
-4	4	4	18.4	-17.5
6	4	4	12.6	11.4
-6	4	4	9.1	8.2
8	4	4	3.2	-3.5
-8	4	4	2.0*	2.4
10	4	4	4.9	-3.6
-10	4	4	1.4*	-0.7
1	5	4	2.2*	2.1
-1	5	4	12.1	-11.5
3	5	4	8.4	6.8
-3	5	4	3.0	-3.4
5	5	4	1.9*	1.4
-5	5	4	50.3	56.7
7	5	4	3.0*	-0.4
-7	5	4	12.4	-10.6
0	6	4	25.4	-24.8
2	6	4	43.7	47.8
-2	6	4	26.1	25.1
4	6	4	18.1	14.8
-4	6	4	14.4	14.6
6	6	4	1.9*	0.7
-6	6	4	6.0	4.7
1	7	4	7.5	-6.2
-1	7	4	4.8	3.9
3	7	4	3.6	-2.7
-3	7	4	4.7	-1.6
5	7	4	11.9	-10.3
-5	7	4	11.0	9.1
7	7	4	5.6	5.7
-7	7	4	4.4	3.7
0	8	4	13.5	12.9
2	8	4	12.4	12.5
-2	8	4	20.0	19.5
4	8	4	3.0*	-0.4
-4	8	4	26.1	-22.9
6	8	4	4.7	-3.4
-6	8	4	1.9*	0.8
1	9	4	12.7	13.0
-1	9	4	8.6	6.8
3	9	4	6.8	6.6
-3	9	4	14.2	15.0
5	9	4	16.3	-17.3
-5	9	4	3.9	3.2
7	9	4	19.3	-20.1
-7	9	4	26.5	26.8
0	10	4	7.1	-7.4
2	10	4	7.4	6.6
-2	10	4	6.2	-4.5
4	10	4	14.8	14.8
-4	10	4	5.2	-5.4
6	10	4	17.3	-16.9
-6	10	4	5.5	5.8
1	11	4	2.4*	2.5
-1	11	4	11.8	-13.6
3	11	4	15.7	17.1
-3	11	4	17.9	22.0
5	11	4	13.7	-11.8
-5	11	4	8.8	7.6
-7	11	4	14.7	15.3
0	12	4	3.3*	2.6
2	12	4	7.3	7.3
-2	12	4	9.6	9.8
4	12	4	12.8	12.7
-4	12	4	2.2*	-2.1
-6	12	4	3.3	3.2
1	13	4	4.2	4.8
-1	13	4	1.8*	2.1
3	13	4	9.3	-8.8
-3	13	4	3.5	-3.3
0	14	4	4.5	6.4
2	14	4	10.7	11.9
-2	14	4	0.8*	5.1
0	0	5	29.7	29.4
2	0	5	5.6	5.0
-2	0	5	16.8	-16.0
4	0	5	2.7*	2.2
-4	0	5	2.7*	-1.2
6	0	5	12.1	-10.6
-6	0	5	2.3*	-1.3
8	0	5	9.2	8.5
-8	0	5	2.6*	2.8
10	0	5	1.5*	1.6
-10	0	5	7.7	-7.4
1	1	5	36.1	37.7
-1	1	5	19.7	-15.7
3	1	5	7.3	-4.9
-3	1	5	15.1	13.9
5	1	5	6.7	5.3
-5	1	5	5.0	3.6
7	1	5	23.2	23.0
-7	1	5	28.4	32.0
9	1	5	2.3	-3.3
-9	1	5	4.8	5.2
0	2	5	23.7	25.8
2	2	5	3.8	2.9
-2	2	5	26.3	28.4
4	2	5	8.1	6.3
-4	2	5	16.6	14.5
6	2	5	3.4	2.4
-6	2	5	19.6	-20.2
8	2	5	5.0	4.7
-8	2	5	10.5	10.4
10	2	5	6.3	5.4
-10	2	5	10.2	9.8
1	3	5	3.3	2.2
-1	3	5	6.0	-3.9
3	3	5	17.3	-16.1
-3	3	5	2.5	-1.0
5	3	5	16.1	15.6
-5	3	5	3.4	3.1
7	3	5	7.1	6.3
-7	3	5	2.4*	-2.7
9	3	5	3.2	2.7
-9	3	5	9.5	9.9
0	4	5	20.7	19.4
2	4	5	24.5	24.2
-2	4	5	14.6	12.7
4	4	5	5.5	-3.7
-4	4	5	17.7	19.1
6	4	5	11.0	10.5
-6	4	5	3.9	-3.0
8	4	5	5.0	-5.2
-8	4	5	7.1	6.3
1	5	5	29.1	28.5
-1	5	5	6.8	7.1
3	5	5	16.6	-15.8
-3	5	5	33.2	-38.6
5	5	5	22.0	22.0
-5	5	5	40.9	43.9
7	5	5	2.9*	1.3
-7	5	5	13.1	12.5
0	6	5	19.5	21.2
2	6	5	8.7	8.0
-2	6	5	3.4	-4.9
4	6	5	19.8	-17.4
-4	6	5	8.4	-8.0
6	6	5	15.9	15.8
-6	6	5	1.9*	0.3
1	7	5	18.0	17.7
-1	7	5	19.0	23.3
3	7	5	18.2	-19.0
-3	7	5	8.5	-8.7
5	7	5	20.3	20.8
-5	7	5	15.2	13.6
7	7	5	14.5	13.1
-7	7	5	14.7	15.5
0	8	5	10.5	10.6
2	8	5	1.9	0.0
-2	8	5	21.2	20.5
4	8	5	2.9*	0.3
-4	8	5	7.3	5.5
6	8	5	3.6	3.4
-6	8	5	20.5	-20.6
1	9	5	6.2	7.1
-1	9	5	16.7	-19.9
3	9	5	5.1	4.4
-3	9	5	14.6	15.1
5	9	5	5.6	-4.7
-5	9	5	8.8	-6.6
7	9	5	12.1	10.6
-7	9	5	9.2	7.3
0	10	5	8.0	7.8
2	10	5	15.7	17.2
-2	10	5	1.7*	2.0
4	10	5	11.2	11.7
-4	10	5	18.2	18.8
6	10	5	14.4	-13.3
-6	10	5	1.8	-0.8
1	11	5	14.9	16.5
-1	11	5	13.0	-15.9
3	11	5	1.5*	-0.1
-3	11	5	4.1	3.6
5	11	5	2.9	-3.0
-5	11	5	1.2*	-0.4
0	12	5	14.7	16.5
2	12	5	6.5	-6.8
-2	12	5	3.5	3.9
4	12	5	1.6*	0.2
-4	12	5	3.1	-4.5
1	13	5	9.7	11.2
-1	13	5	13.6	15.1
0	0	6	6.5	6.9
2	0	6	10.2	9.3
-2	0	6	7.4	-6.2
4	0	6	3.9	3.0
-4	0	6	15.5	14.8
6	0	6	23.2	-23.5
-6	0	6	7.4	5.4
8	0	6	19.7	21.9
-8	0	6	6.6	-6.1
1	1	6	8.2	6.4
-1	1	6	18.5	-16.4
3	1	6	3.9	3.7
-3	1	6	12.8	-10.7
5	1	6	11.9	-9.8
-5	1	6	18.9	-17.6
7	1	6	9.7	9.2
-7	1	6	2.4*	1.3
9	1	6	5.7	-5.7
-9	1	6	2.0	2.7
0	2	6	8.6	-7.7
2	2	6	27.2	-28.6
-2	2	6	18.2	19.2
4	2	6	11.3	10.9
-4	2	6	2.5*	1.9
6	2	6	5.1	-4.4
-6	2	6	14.5	-14.7
8	2	6	3.4	3.2
-8	2	6	9.5	-10.1
1	3	6	22.2	-22.1
-1	3	6	33.2	36.6
3	3	6	7.9	-6.6
-3	3	6	12.8	-11.7
5	3	6	25.6	27.0
-5	3	6	9.2	-7.8
7	3	6	2.1*	-1.8
-7	3	6	2.2*	1.8
9	3	6	7.9	-8.2
-9	3	6	5.6	5.7
0	4	6	3.4	-1.4
2	4	6	23.8	-23.1
-2	4	6	14.6	13.0
4	4	6	2.5*	0.3
-4	4	6	14.4	-15.2
6	4	6	2.9	2.8
-6	4	6	3.4	-3.4
8	4	6	6.4	-5.2
-8	4	6	3.3	-4.1
1	5	6	3.8	-4.7
-1	5	6	21.0	25.7
3	5	6	5.1	-4.0
-3	5	6	45.2	-51.4
5	5	6	11.1	9.6
-5	5	6	9.5	8.4
7	5	6	9.0	-9.2
-7	5	6	5.9	6.5
0	6	6	3.9*	-0.5
2	6	6	6.3	6.4
-2	6	6	8.2	7.1
4	6	6	2.9*	-2.8
-4	6	6	2.9*	2.9
6	6	6	5.3	-4.6
-6	6	6	5.2	4.3
1	7	6	14.8	-14.9
-1	7	6	5.9	6.6
3	7	6	1.9*	-0.3
-3	7	6	17.8	-19.0
5	7	6	5.6	5.6
-5	7	6	5.1	-4.5
7	7	6	2.7	-3.0
-7	7	6	13.1	-10.3
0	8	6	9.4	-9.3
2	8	6	12.6	-13.5
-2	8	6	16.5	16.5
4	8	6	6.6	6.3
-4	8	6	10.0	8.8
6	8	6	1.8	-1.7
-6	8	6	17.4	-15.4
1	9	6	2.2*	-1.3
-1	9	6	5.7	4.8
3	9	6	1.6*	-1.0
-3	9	6	3.6	2.8
5	9	6	5.0	3.7
-5	9	6	15.6	-13.2
0	10	6	3.1*	2.3
2	10	6	10.5	-10.6
-2	10	6	4.0	-3.8
4	10	6	1.9*	1.2
-4	10	6	4.1	-5.4
1	11	6	6.7	8.2
-1	11	6	1.6*	-3.5
3	11	6	1.1*	0.2
-3	11	6	5.6	-4.7
0	12	6	1.8*	-0.7
0	0	7	16.2	-15.8
2	0	7	11.4	-9.9
-2	0	7	7.4	-6.3
4	0	7	7.8	-7.1
04	0	7	7.0	-6.5
6	0	7	3.2	-2.8
-6	0	7	12.1	-12.6
8	0	7	1.3*	1.6
-8	0	7	4.4	-3.0
1	1	7	7.7	6.2
-1	1	7	9.9	-9.1
3	1	7	6.7	-6.1
-3	1	7	14.1	14.0
5	1	7	4.3	-4.3
-5	1	7	22.0	-24.6
7	1	7	4.9	5.2
-7	1	7	3.2	-2.5
0	2	7	24.7	-27.3
2	2	7	4.7	4.4
-2	2	7	5.6	-4.5
4	2	7	2.4*	-2.0
-4	2	7	15.9	16.0
6	2	7	3.3	-3.4
-6	2	7	4.0	-4.2
-8	2	7	10.5	-10.8
1	3	7	11.9	-10.5
-1	3	7	12.0	-11.6
3	3	7	1.8*	1.6
-3	3	7	3.7	-3.4
5	3	7	4.8	-4.4
-5	3	7	9.9	-9.5
7	3	7	5.5	-5.8
-7	3	7	14.4	-14.0
0	4	7	20.7	-22.0
2	4	7	6.7	6.7
-2	4	7	5.8	4.9
4	4	7	7.7	-6.5
-4	4	7	2.3*	2.1
6	4	7	1.5*	0.4
-6	4	7	1.6*	-0.7
1	5	7	15.0	-15.2
-1	5	7	20.7	24.4
3	5	7	4.3	-3.4
-3	5	7	15.7	-17.7
5	5	7	4.2	4.1
-5	5	7	16.4	-17.4
-7	5	7	8.4	3.4
0	6	7	21.5	-23.9
2	6	7	5.1	-4.9
-2	6	7	8.3	8.4
4	6	7	5.6	-5.6
-4	6	7	10.5	-10.6
6	6	7	2.1	2.5
-6	6	7	13.7	-12.9
1	7	7	12.4	-12.9
-1	7	7	6.1	7.2
3	7	7	3.3	3.0
-3	7	7	4.3	4.2
5	7	7	6.7	5.1
-5	7	7	10.2	-8.8
0	8	7	20.8	-24.0
2	8	7	4.6	4.5
-2	8	7	5.7	-5.3
4	8	7	2.7	-2.8
-4	8	7	15.0	15.0
1	9	7	5.0	6.1
-1	9	7	14.3	-18.3
3	9	7	3.6	-3.4
-3	9	7	6.7	5.1
0	10	7	2.2	-3.1*
2	10	7	4.2	4.2
-2	10	7	7.9	-7.4
0	0	8	16.1	18.3
2	0	8	3.4	-1.4
-2	0	8	17.7	-19.6
4	0	8	3.6	-4.3
-4	0	8	9.8	9.9
6	0	8	3.2	2.9
-6	0	8	7.4	6.7
1	1	8	13.2	13.1
-1	1	8	9.5	-8.5
3	1	8	13.9	-15.9
-3	1	8	6.1	5.0
5	1	8	2.0	2.2
-5	1	8	2.5	1.0
0	2	8	6.5	-5.1
2	2	8	4.5	4.1
-2	2	8	18.3	-20.4
4	2	8	5.8	5.6
-4	2	8	11.9	12.8
6	2	8	5.7	-5.3
-6	2	8	3.9	3.3
1	3	8	6.6	-6.0
-1	3	8	2.3	1.3
3	3	8	6.5	6.2
-3	3	8	8.7	8.9
5	3	8	7.6	6.8
-5	3	8	11.5	9.9
0	4	8	12.0	-12.0
2	4	8	3.7	3.2
-2	4	8	5.5	-5.2
4	4	8	4.5	4.1
-4	4	8	3.2	2.6
-6	4	8	7.7	-7.5
1	5	8	12.5	-12.3
-1	5	8	16.1	19.4
3	5	8	2.1	-2.4
-3	5	8	3.6	-4.2
5	5	8	5.3	4.7
-5	5	8	2.3	-2.6
0	6	8	2.8*	-0.3
2	6	8	6.3	7.3
-2	6	8	5.0	-5.1
4	6	8	3.3	-4.0
-4	6	8	6.2	6.1
1	7	8	1.5*	-1.8
-1	7	8	1.6*	-0.7
3	7	8	3.2	-2.3
-3	7	8	4.8	-4.7
2	8	8	5.6	6.9
-2	8	8	16.1	-18.6
0	0	9	7.5	7.8
2	0	9	1.6*	-1.8
-2	0	9	4.1	-3.6
-4	0	9	1.1*	-1.9
1	1	9	2.2	2.3
-1	4	9	1.5*	2.0
3	1	9	1.1*	0.8
-3	1	9	7.7	7.4
0	2	9	10.8	11.2
2	2	9	8.4	8.4
-2	2	9	7.1	-6.9
1	3	9	3.7	-2.9
-1	3	9	5.3	5.9
3	3	9	4.5	5.4
-3	3	9	7.2	-7.7
0	4	9	1.6*	1.0
2	4	9	10.7	12.7
-2	4	9	5.3	4.8

1962) reduced the R index to 0·13. Of the 874 observed reflexions, 16 strong low-orders were significantly weaker than the calculated values. This was assumed to be due to extinction. Therefore these reflexions (which, together with the unobserved ones, are marked * in Table 2) were omitted from the three terminal cycles of full-matrix anisotropic least-squares refinement computing on an IBM 7090 with the local version (Shiono, 1963) of the Busing, Martin & Levy (1962) program. The function minimized was $\Sigma\omega(F_o - kF_c)^2$ using the Hughes (1941) weighting scheme with $|F_{\text{min}}| = 2{\cdot}5$. The scattering factors of Berghuis, Haanappel, Potters, Loopstra, MacGillavry & Veenendaal (1955) were used. The final unweighted R index was 0·097. This value does not include the unobserved reflexions and the 16 strong low-orders mentioned above. The maximum final parameter shift was 0·03σ.

The hydrogen atom peaks were sought on difference Fourier syntheses, but only three of the six in the asymmetric unit could be directly located. The inclusion of these three atoms slightly improved the agreement.

The final atomic parameters and their estimated standard deviations from the least-squares refinement are given in Table 1. The observed and calculated structure factors are given in Table 2. There was no evidence indicating that the symmetry of the structure was other than $C2/m$ with the organic molecule and one water molecule in special positions and the remaining water molecule in the general position. A composite electron density map with a corresponding formula unit and key to the atomic notation is shown in Fig. 1.

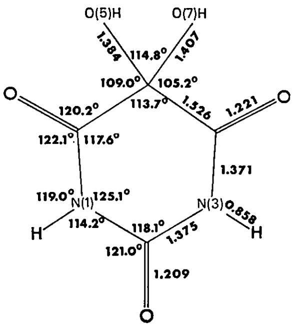


Fig. 2. The 5,5-dihydroxybarbituric acid molecule with bond lengths and angles.

The structure of the molecule

As anticipated, alloxan tetrahydrate is misnamed and is the trihydrate of 5,5-dihydroxybarbituric acid. The molecule has a crystallographic plane normal to the pyrimidine ring and passing through atoms O(2), C(2), C(5), O(5), O(7) (Fig. 1). One of the three water molecules, $W(2)$, lies on the twofold axis parallel to **b**.

Structural data were calculated with programs written by Chu (1963) for the IBM 1620 computer. The bond distances and angles in the molecules are given in Table 3 and Fig. 2.

The two independent C–N distances are not significantly different and have a mean value of 1·373 Å. Similarly the two C=O distances are not significantly different from the mean value of 1·215 Å. Both these bond lengths are consistent with those observed in other pyrimidine derivatives. The two C–O(H) bonds have a mean value of 1·395 Å. This is significantly shorter than the value of 1·43 Å normally associated with the single C–O(H) bond, in carbohydrates for example. On the other hand, the adjacent C–C bonds of 1·526 Å correspond closely to a single-bond length for an sp^2–sp^3 bond, so it is unlikely that there is any π interaction between the C–OH bonds and the aromatic part of the pyrimidine ring.

An analysis of the planarity of the ring and its substituents is given in Table 4. These results show that with the exception of C(5), the ring atoms are coplanar within 0·018 Å. C(5) is out of this plane by 0·214 Å and in consequence the hydroxyl oxygen atoms are unsymmetrically disposed above and below the five ring atoms. The carbonyl oxygen atoms are displaced out of the plane of the ring in the opposite direction to C(5), as is consistent with a minimum strain distortion from the planarity of the pyrimidine ring.

Table 3. *Valence bond lengths and bond angles*

Estimated standard deviations in parentheses

Distances		Angles	
C(2)–N(3,1)	1·375(5) Å	N(1)–C(2)–N(3)	118·1(5)°
C(4,6)–N(3,1)	1·371(4)	C(2)–N(3,1)–C(4,6)	125·1(3)
C(4,6)–C(5)	1·526(5)	C(5)–C(4,6)–N(3,1)	117·6(3)
		C(4)–C(5)–C(6)	113·7(4)
C(2)–O(2)	1·209(6)	N(3,1)–C(2)–O(2)	121·0(4)
C(4,6)–O(4,6)	1·221(4)	N(3,1)–C(4,6)–O(4,6)	122·1(3)
C(5)–O(5)	1·384(5)	C(5)–C(4,6)–O(4),6	120·2(3)
C(5)–O(7)	1·407(5)	C(4,6)–C(5)–O(5)	109·0(3)
		C(4,6)–C(5)–O(7)	105·2(3)
		O(5)–C(5)–O(7)	114·8(3)
N(3,1)–H(N3,1)	0·86 Å	C(2)–N(3,1)–H(N3,1)	114°
W(1)–H(1W1)	0·96	C(4,6)–N(3,1)–H(N3,1)	119
W(2)–H,H′(W2)	0·94	H(W2)–W(2)–H′(W2)	106

Table 4. *Distances of atoms from two least-squares planes through the molecule*

The least-squares method of Schomaker *et al.* (1959) was used. Equations of planes with respect to the crystallographic axes (coordinates and d in Å); $ax+by+cz=d$.

	Plane through all six ring atoms $a=0{\cdot}7218$, $b=0{\cdot}0000$, $c=0{\cdot}6826$, $d=1{\cdot}8608$		Plane through all ring atoms except C(5) $a=0{\cdot}6845$, $b=0{\cdot}0000$, $c=0{\cdot}7200$, $d=1{\cdot}7539$	
	Distances to plane for atoms forming ——— not forming the plane.		Distances to plane for atoms forming ——— not forming the plane.	
N(1,3)	0·015 Å	———	0·014 Å	———
C(2)	0·020	———	−0·018	———
C(4,6)	−0·075	———	−0·005	———
C(5)	0·101	———	———	0·214 Å
O(2)	———	0·014 Å	———	−0·087
O(4,6)	———	−0·239	———	−0·139
O(5)	———	−0·813	———	−0·644
O(7)	———	1·450	———	1·582

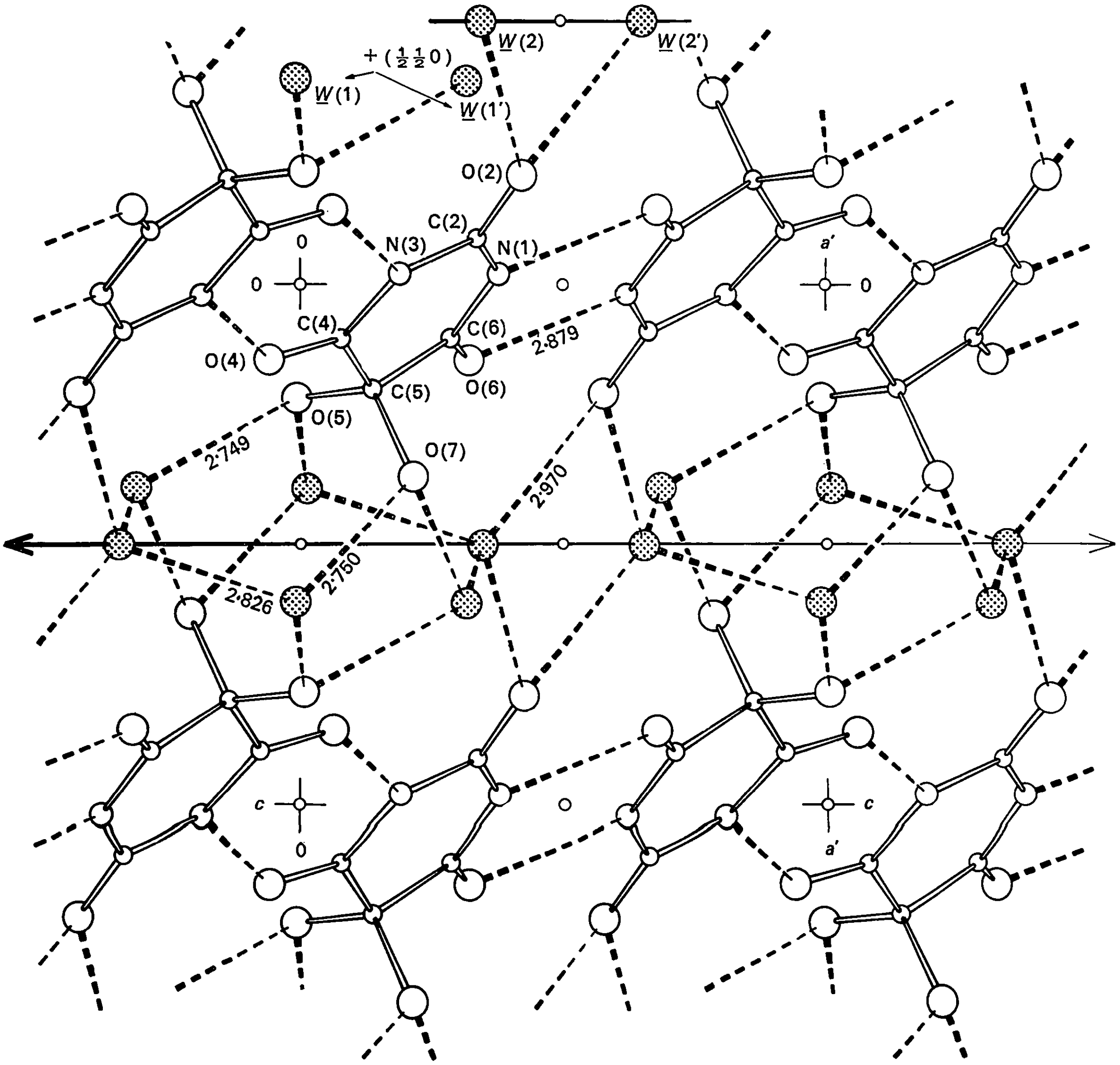
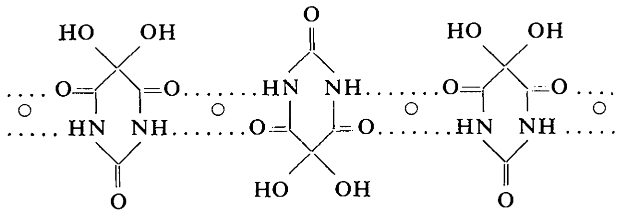


Fig. 3. A view in the [110] direction showing the hydrogen-bonding scheme in a buckled sheet of the structure. Broken lines represent hydrogen bonds. The hydrogen atoms are omitted for clarity. Since β is very near to 90° the principal axes have been treated as orthogonal while constructing this projection.

The hydrogen bonding

In this structure, all oxygen, nitrogen and hydrogen atoms participate in the hydrogen bonding, the stereochemistry of which is given in Table 5. The dihydroxybarbituric acid molecules are hydrogen bonded to each other in a continuous ribbon across the centers of symmetry in the *b* axis direction as shown diagrammatically (IV) and in Fig. 3.



(IV) (○ Indicates centers of symmetry)

The hydrogen bonding is through the NH and CO groups in the 1, 3 and 4, 6 positions and the N(H) · · · O distance is 2·879 Å. The pyrimidine rings of alternate molecules along the chain lie in parallel planes separated by 0·23 Å. The ribbon type of hydrogen bonding is common in the crystal structures of pyrimidine derivatives generally, but exactly the same scheme of straight ribbons is possible, of course, only with molecules having the same pattern of substitution in positions 1, 3, 4 and 6. Although this requirement is met by all barbituric acid derivatives, of the crystal structures hitherto reported only in 5,5-diethylbarbituric acid, *i.e.* veronal (Bertinotti, Bonamico, Braibanti, Coppola & Giacomello, 1959), is the ribbon structure as represented in (IV).

The water molecules lie between these ribbons of hydrogen-bonded pyrimidine molecules and associate

Table 5. *Geometry of hydrogen bonds*

In terms of atoms of the asymmetric unit only, plus equipoints
Solid lines: valence bonds, dotted lines: hydrogen bonds

Hydrogen bond	Basic geometry		Further angles	
O(2) · · · H–*W*(2) x, y, z $x, \bar{y}, z$	d(O · · · *W*) d(O · · · H) d(H–*W*) Angle (O · · · H–*W*)	2·970 Å 2·04 0·94 177°	C(2)=O · · · *W* *W* · · · O · · · *W*	135·0° 78·7
O(4) · · · H–N(3) $\frac{1}{2}-x, \frac{1}{2}-y, \bar{z}$	d(O · · · N) d(O · · · H) d(H–N) Angle (O · · · H–N)	2·879 Å 2·05 0·86 161°	C(4)=O · · · N C(4)–N · · · O	126·8° 110·9
O(5) · · · *W*(1) $\bar{x}, y, \bar{z}$ $\bar{x}, \bar{y}, \bar{z}$	d(O · · · *W*) hydrogen atom could not be located	2·749 Å	C(5)–O · · · *W* *W* · · · O · · · *W*	123·8° 91·9
O(7) · · · *W*(1) $x, y, 1+z$ $x, \bar{y}, 1+z$	d(O · · · *W*) hydrogen atom could not be located	2·750 Å	C(5)–O · · · *W* *W* · · · O · · · *W*	118·1° 91·9
W(2) · · · H–*W*(1) $\frac{1}{2}-x, \frac{1}{2}-y, -1-z$ $\frac{1}{2}+x, \frac{1}{2}-y, z$	d(*W* · · · *W*) d(*W* · · · H) d(H–*W*) Angle (*W* · · · H–*W*)	2·826 Å 2·03 0·96 135°	*W*(1) · · · *W*(2) · · · *W*(1)	72·8°

Other hydrogen bond angles at water molecules (requiring a different identification through equipoints):

W(1)	O(5) · · · *W*(1) · · · O(7) $\bar{x}, y, \bar{z}$	 $x, y, -1+z$	84·3°
	O(5) · · · *W*(1) · · · *W*(2) $\bar{x}, y, \bar{z}$	 $\frac{1}{2}-x, \frac{1}{2}-y, -1-z$	116·5°
	O(7) · · · *W*(1) · · · *W*(2) $x, y, -1+z$	 $\frac{1}{2}-x, \frac{1}{2}-y, -1-z$	119·6°
W(2)	O(2) · · · *W*(2) · · · O(2) x, y, z	 $1-x, y, -1-z$	101·3°
	O(2) · · · *W*(2) · · · *W*(1) x, y, z	 $\frac{1}{2}-x, \frac{1}{2}-y, -1-z$	126·1° (2)
	O(2) · · · *W*(2) · · · *W*(1) $1-x, y, -1-z$	 $\frac{1}{2}+x, \frac{1}{2}-y, z$	
	O(2) · · *W*(2) · · · *W*(1) x, y, z	 $\frac{1}{2}+x, \frac{1}{2}-y, z$	115·5° (2)
	O(2) · · · *W*(2) · · · *W*(1) $1-x, y, -1-z$	 $\frac{1}{2}-x, \frac{1}{2}-y, -1-z$	

them into buckled sheets by hydrogen bonding through the dihydroxy groups and the third carbonyl oxygen atom, as shown in Fig. 3. The buckled sheets lie between adjacent (201) planes as shown in Fig. 4. There is no hydrogen bonding between these sheets.

Of the water molecules, those in the general position *W*(1) are engaged in three hydrogen bonds, and those in the special position *W*(2) have four hydrogen bonds. The *W*(1) molecules form two bonds to the hydroxyl oxygen atoms of 2·749 and 2·750 Å, thereby linking the O(5) and O(7) atoms of molecules in adjacent ribbons. The third hydrogen bond is to a *W*(2) water molecule at 2·826 Å. Although the coordination is threefold, it is not trigonal planar, as shown by the O · · · O · · · O angles of 84·3°, 116·5° and 119·6°. The *W*(1) oxygen atom is 1·009 Å out of the plane of O(5), O(7) and *W*(2) and is therefore more nearly in a threefold pyramidal hydrogen-bond configuration.

The *W*(2) water molecule links the carbonyl oxygen atoms, O(2), of two molecules in adjacent ribbons by hydrogen bonds of 2·970 Å. The other two hydrogen bonds are to *W*(1) water molecules at 2·826 Å. These four bonds are related in pairs by the twofold axis parallel to **b**. The coordination is very distorted from tetrahedral as shown by the variation in the O · · · O · · · O angles from 72·8° to 126·1°. Three of the oxygen atoms of the molecule, O(2), O(5) and O(7), are involved in a pair of hydrogen bonds which are related by the crystallographic mirror symmetry. The remaining oxygen atoms O(4) and O(6), which are symmetry related, accept a single hydrogen bond from the NH groups.

Three symmetry independent hydrogen atoms in general positions were directly located; one on *W*(1), one on *W*(2) and one on the nitrogen atom. The remaining three, one on *W*(1) in general position and the other two on the two hydroxyl oxygen atoms in

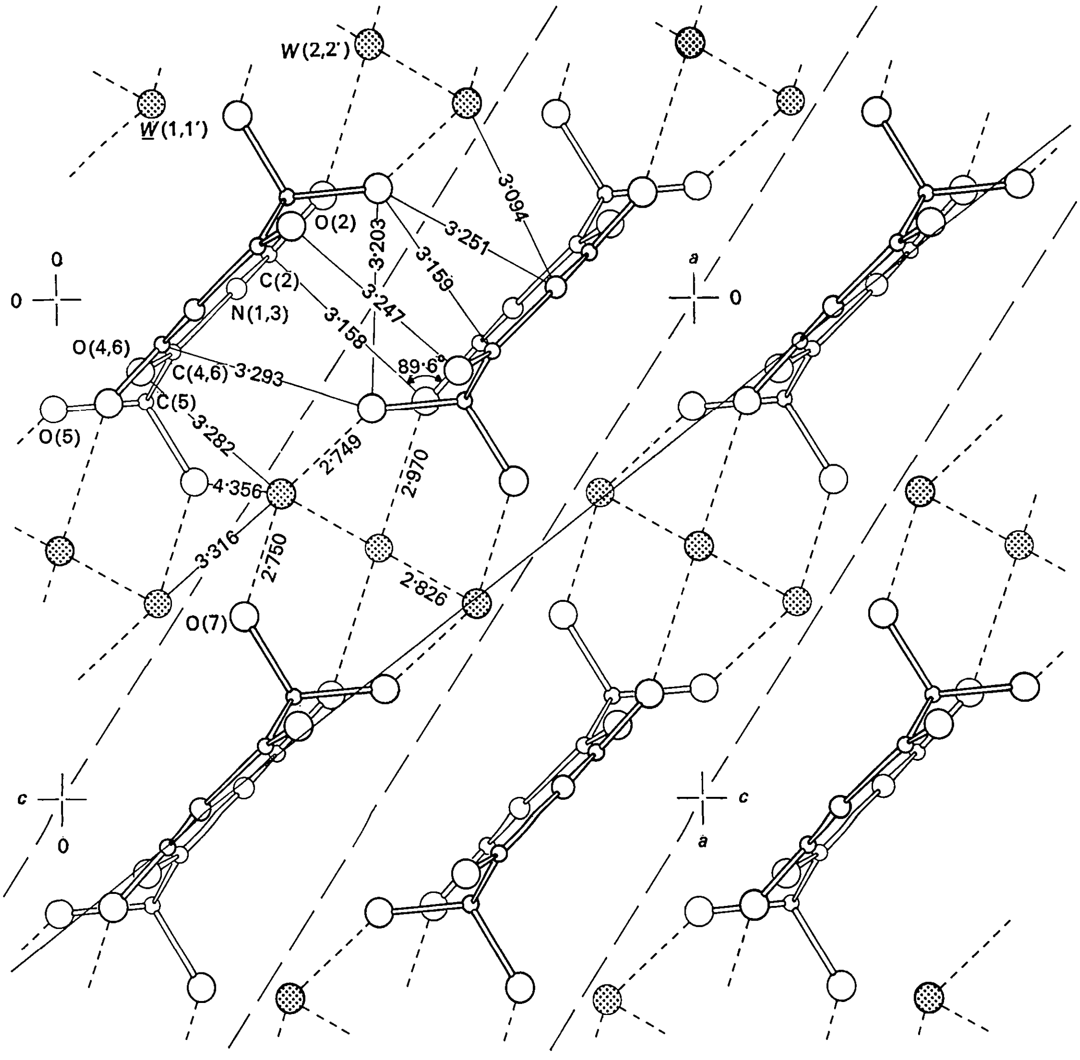
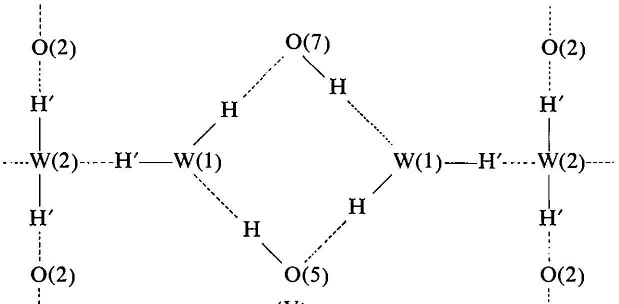
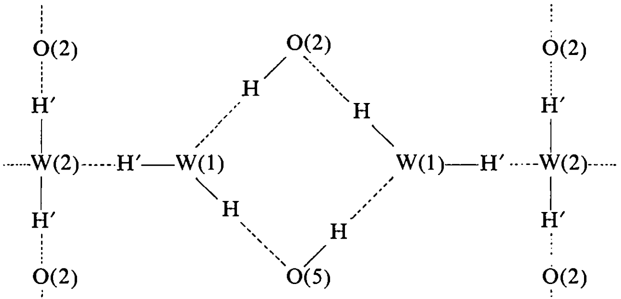


Fig. 4. A view down the *b* axis showing most of the hydrogen bonds (broken lines) and other intermolecular distances. The set of three parallel thin broken lines running across the figure represents traces of adjacent (201) planes while the long thin line from left bottom to right top is the trace of a net-plane halfway between adjacent (202) planes. Hydrogen atoms are omitted for clarity.

special positions, must be disordered in accordance with the symmetry of the crystal structure. The hydrogen bonding involving the water molecules can be represented schematically as a statistical disorder of (V) and (VI).



(V)



(VI)

The hydrogen atoms which were directly located are indicated by the primes.

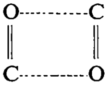
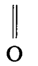
The intermolecular distances less than 3·3 Å, other than those of the hydrogen bonds, are given in Table 6 and Fig. 4. One interesting feature is the configuration  $\begin{array}{ccc} O & \cdots & C \\ \| & & \| \\ C & \cdots & O \end{array}$ formed across a center of symmetry by parallel but oppositely oriented C(2)=O(2) groups of two molecules in adjacent sheets. With two C(2) ---O(2) distances of 3·158 Å and all angles C=O --- C and O --- C=O close to 90° this grouping is very similar to intermolecular carbonyl–carbonyl arrangements observed in the crystal structure of 5-hydroxyiminobarbituric acid monohydrate (Craven & Mascarenhas, 1964) and 5-nitrobarbituric acid trihydrate (Craven, Martinez-Carrera & Jeffrey, 1964). The exceptionally short intermolecular  $\begin{array}{l} C\cdots O{=}C \\ \| \\ O \end{array}$ distances found in the anhydrous crystal structures of alloxan (Bolton, 1964), barbituric acid (Bolton, 1963) and parabanic acid (Davies & Blum, 1955) are not observed.

Table 6. *Other intermolecular distances less than* 3·3 Å (*excluding hydrogen atoms*)

i	*j* with equipoint indication	d_{ij}
C(2)	O(2) $1-x, y, \bar{z}$	3·158 Å
C(2)	O(5) $\bar{x}, y, \bar{z}$	3·293
C(4)	O(5) $\bar{x}, y, \bar{z}$	3·159
N(3)	O(5) $\bar{x}, y, \bar{z}$	3·251
N(3)	*W*(1) x, y, z	3·094
O(4)	O(4) $\bar{x}, y, \bar{z}$	3·247
O(4)	*W*(1) $\frac{1}{2}-x, \frac{1}{2}-y, \bar{z}$	3·282
O(5)	O(5) $\bar{x}, y, \bar{z}$	3·203

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