

the present molecule is too simple to distinguish the out-of-plane oxygen vibration from the rigid body libration of the whole molecule.

### 5. Concluding remarks

In the present calculations, ordinary spherical scattering factors were used for the carbon and hydrogen atoms, and the effect of bond scattering factor (McWeeny, 1952) and the possibility of the charge transfer as a result of the hydrogen bond (Tsubomura, 1954) were completely neglected. In this respect, the present treatment is still too naive to discuss the distribution of valence electrons. Also, an  $R$  value of around 10% is sufficient to determine the atomic positions, but not enough to discuss the effect of bonding. This will be the limit of the ordinary photographic measurement of diffraction intensity.

One aim of this paper, however, is to show that even at this level of accuracy the introduction of the aspherical atomic scattering factor can improve the results of structure analyses.

In the present study, the changes in bond distances and angles were negligible. However, this result should not be considered to be general. If an atom is not centrosymmetric, the imaginary component in equation (10) will introduce the shift of the positional parameter, as discussed by Dawson (1964a).

It can be seen from Table 6, that there still remains a small but systematic discrepancy of the  $U_{11}$  component of the oxygen atom. This may be due to the effect of bonding.

In order to clarify these points, accurate counter measurements at various temperatures are now being planned.

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## The Crystal Structure of Thymine

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The crystals of thymine anhydrate are monoclinic with the space group  $P2_1/c$ . The unit-cell dimensions have been reported as follows:  $a=12.87$ ,  $b=6.83$ ,  $c=6.70$  Å,  $\beta=105^\circ$  and  $Z=4$ . The structure was determined and refined by the three-dimensional least-squares method. The final  $R$  index for 724 observed reflections is 0.149 and the standard deviations in the positional parameters are about 0.011 Å. Pairs of molecules related by the twofold screw axis are connected by the two N-H...O=C hydrogen bonds and they form infinite chains along the  $b$  axis.

### Introduction

Thymine is an essential component of deoxyribonucleic acid (DNA) molecule, and its structure is of par-

ticular importance in understanding the mechanism of the biological functions of DNA. The crystal of thymine monohydrate has been analysed by Gerdil (1961), but only the crystal data of thymine anhydrate are re-

ported by Furberg & Hordvik (1956) as follows;  $a=12.87$ ,  $b=6.83$ ,  $c=6.70$  Å,  $\beta=105^\circ$  and  $Z=4$ . Space group  $P2_1/c$ .

The crystal structure analysis of thymine anhydrate has been made in order to obtain precise information concerning the bond length, the mode of hydrogen bonding and the packing of molecules in the crystal.

### Experimental

#### Unit cell and space group

Single crystals of thymine were grown by slow evaporation of aqueous solutions containing 10% ethanol at room temperature. They were needles elongated along the  $b$  axis, the well-developed planes being (001) and (100). A single crystal having dimensions of  $0.1 \times 1.0 \times 0.2$  mm was used for taking Weissenberg photographs around the  $b$  axis. A fragment having dimensions of  $0.1 \times 0.1 \times 0.2$  mm obtained by cutting

that crystal was used for taking Weissenberg photographs around the  $c$  axis.

The previous results on the unit-cell dimensions and space group were confirmed by oscillation and Weissenberg photographs. The density measured by the flotation method, in a cyclohexane and carbon tetrachloride mixture at  $25^\circ\text{C}$ , was  $1.455 \pm 0.005$  g.cm $^{-3}$ . The calculated number of molecules per unit cell was 3.97, therefore  $Z=4$ .

#### Collection of intensity data

The intensity data were obtained from equi-inclination vertically and horizontally integrated Weissenberg photographs taken with nickel filtered  $\text{Cu K}\alpha$  radiation. The multiple film technique was used and the intensities were estimated visually by comparison with a calibrated scale. Data were collected from the zero to fourth layers around the  $b$  and  $c$  axes, respectively.

Table 1. Final positional and anisotropic thermal parameters and (below) their standard deviations

[ $s(x)$ ,  $s(y)$ ,  $s(z)$  in Å and  $S(B_{ij})$  in Å $^2$ ].

ATOM	X	Y	Z	B11	B22	B33	B12	B13	B23
C 1	0.5835	0.4897	0.7356	0.00195	0.01493	0.01642	0.00062	0.00676	0.00180
C 2	0.7443	0.6604	0.7230	0.00286	0.01818	0.01623	-0.00032	0.00441	-0.00639
C 3	0.7984	0.4906	0.7082	0.00415	0.01496	0.01669	-0.00326	0.00337	0.00585
C 4	0.9138	0.4893	0.6905	0.00397	0.02585	0.03175	0.00194	0.00955	-0.00192
C 5	0.7413	0.3026	0.7036	0.00357	0.01099	0.01572	0.00146	0.00533	0.00168
N 1	0.6371	0.6536	0.7379	0.00559	0.01556	0.01233	-0.00209	0.00646	0.00301
N 2	0.6341	0.3210	0.7174	0.00516	0.01593	0.01198	-0.00122	0.00437	0.00314
O 1	0.4878	0.4891	0.7430	0.00593	0.01212	0.01939	-0.00011	0.00782	-0.00243
O 2	0.7810	0.1459	0.6963	0.00345	0.00788	0.01730	0.00360	0.00473	0.00280

#### ESTIMATED STANDARD DEVIATIONS

ATOM	S(X)	S(Y)	S(Z)	S(B11)	S(B22)	S(B33)	S(B12)	S(B13)	S(B23)
C 1	0.0096	0.0120	0.0108	0.00060	0.00262	0.00268	0.00223	0.00205	0.00470
C 2	0.0110	0.0129	0.0115	0.00069	0.00303	0.00273	0.00243	0.00221	0.00508
C 3	0.0116	0.0125	0.0118	0.00077	0.00285	0.00281	0.00263	0.00236	0.00513
C 4	0.0131	0.0161	0.0153	0.00082	0.00405	0.00432	0.00325	0.00307	0.00731
C 5	0.0110	0.0112	0.0111	0.00072	0.00249	0.00269	0.00226	0.00222	0.00447
N 1	0.0103	0.0105	0.0092	0.00076	0.00247	0.00222	0.00229	0.00207	0.00413
N 2	0.0101	0.0105	0.0092	0.00073	0.00247	0.00216	0.00222	0.00201	0.00406
O 1	0.0090	0.0084	0.0090	0.00063	0.00184	0.00205	0.00189	0.00183	0.00363
O 2	0.0074	0.0073	0.0076	0.00050	0.00158	0.00191	0.00154	0.00156	0.00309

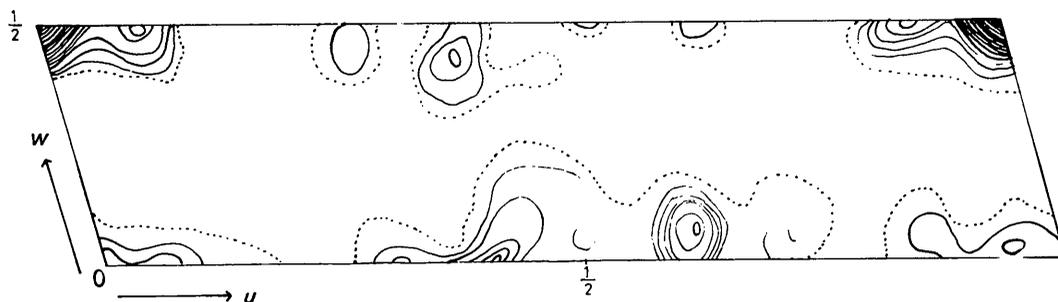


Fig. 1. Sharpened Patterson section through  $(0, \frac{1}{2}, 0)$ . Here  $u$  and  $w$  refer to the  $x$  and  $z$  axes, respectively. Contours are drawn at equal but arbitrary intervals, beginning with the zero contour (dashed line).

Table 2. *Observed and calculated structure factors*The three columns in each group contain the values, reading from left to right of  $k$ ,  $10 F_o$  and  $10 F_c$ .

K	FO	FC	K	FO	FC	K	FO	FC	K	FO	FC	K	FO	FC	K	FO	FC	K	FO	FC
H <sub>1</sub> L <sub>1</sub> =14 0	4	17 13	3 38 35	6 34 30	0 0 -17	2 47 40	0 15 -28	H <sub>1</sub> L <sub>1</sub> =0 5	K 10 -28	3 44 -49										
0 29 38	5 30 32	H <sub>1</sub> L <sub>1</sub> =7 1	7 13 5	0 0 -11	3 0 2	1 50 -39	1 95 77	H <sub>1</sub> L <sub>1</sub> =-6 6	4 12 -28											
2 18 25	H <sub>1</sub> L <sub>1</sub> =10 7	4 21 23	8 34 30	2 39 43	0 21 23	2 42 23	2 21 16	0 92 -91	H <sub>1</sub> L <sub>1</sub> =10 7											
4 3 5	1 20 25	2 51 -48	H <sub>1</sub> L <sub>1</sub> =-2 2	3 0 0	5 0 -11	3 0 10	3 0 10	1 0 -6	1 7 24											
H <sub>1</sub> L <sub>1</sub> =13 0	2 0 2	3 0 0	5 109 104	4 13 0	6 90 82	4 40 31	4 22 -17	2 0 -8	2 0 6											
0 31 -38	3 81 -81	4 29 28	1 106 98	H <sub>1</sub> L <sub>1</sub> =12 2	7 21 23	H <sub>1</sub> L <sub>1</sub> =3 4	H <sub>1</sub> L <sub>1</sub> =-1 5	3 0 -7	3 25 -29											
2 15 -15	4 36 -63	5 68 -63	2 235-255	0 0 -11	0 57 46	0 57 46	1 76 -55	4 8 5	H <sub>1</sub> L <sub>1</sub> =11 7											
4 19 -30	H <sub>1</sub> L <sub>1</sub> =-9 1	H <sub>1</sub> L <sub>1</sub> =8 1	3 52 44	1 0 14	0 76 76	1 0 14	0 76 76	1 0 14	H <sub>1</sub> L <sub>1</sub> =-7 6											
H <sub>1</sub> L <sub>1</sub> =12 0	1 47 47	1 29 28	4 147-129	2 16 -22	1 0 0	2 116-106	3 79 71	n 7n 73	2 n -25											
0 25 32	2 57 47	2 31 28	5 59 -44	H <sub>1</sub> L <sub>1</sub> =14 2	2 99 -71	3 0 -16	4 16 11	1 38 40	3 13 20											
2 40 35	3 287 217	3 41 -41	6 39 14	0 15 -24	3 21 28	4 73 -73	H <sub>1</sub> L <sub>1</sub> =-2 5	2 40 -33	H <sub>1</sub> L <sub>1</sub> =12 7											
4 29 39	4 5 -6	4 12 9	7 13 2	H <sub>1</sub> L <sub>1</sub> =10 3	4 62 -43	H <sub>1</sub> L <sub>1</sub> =4 4	0 44 49	3 0 3	1 4 -7											
H <sub>1</sub> L <sub>1</sub> =11 0	H <sub>1</sub> L <sub>1</sub> =-8 1	5 0 12	8 35 -28	1 110-111	H <sub>1</sub> L <sub>1</sub> =-2 4	0 47 35	2 7 2	4 19 -12	2 0 2											
0 25 21	1 34 -58	6 25 -31	H <sub>1</sub> L <sub>1</sub> =-1 2	2 66 -50	0 11 -8	1 0 5	3 0 -16	H <sub>1</sub> L <sub>1</sub> =-8 6	H <sub>1</sub> L <sub>1</sub> =2 7											
2 46 -44	2 0 0	H <sub>1</sub> L <sub>1</sub> =9 1	0 35 -24	3 50 -37	1 80 -72	2 53 41	4 29 -29	0 0 -10	4 6 -10											
4 17 -8	3 34 -9	1 53 -53	1 98 80	4 43 33	2 140 138	3 0 -3	H <sub>1</sub> L <sub>1</sub> =-3 5	1 0 2	H <sub>1</sub> L <sub>1</sub> =2 7											
H <sub>1</sub> L <sub>1</sub> =10 0	4 29 -2	3 44 -43	2 48 67	5 81 -78	3 25 13	2 26 13	4 30 3	1 29 -26	2 0 11											
0 20 13	5 0 -1	3 152-146	3 31 -27	6 69 63	4 77 73	H <sub>1</sub> L <sub>1</sub> =5 4	2 25-18	3 19 31	2 0 11											
1 0 -22	6 16 -21	4 24 -27	4 66 50	H <sub>1</sub> L <sub>1</sub> =-1 3	5 45 35	0 0 -16	3 88 -77	4 6 -6	3 20 -11											
2 102 108	H <sub>1</sub> L <sub>1</sub> =-7 1	H <sub>1</sub> L <sub>1</sub> =10 1	5 0 6	1 133 130	H <sub>1</sub> L <sub>1</sub> =-3 4	1 38 28	4 13 11	H <sub>1</sub> L <sub>1</sub> =-9 6	H <sub>1</sub> L <sub>1</sub> =3 7											
3 32 -31	1 181 93	2 23 -23	6 0 6	2 66 -49	0 65 -60	2 15 -1	0 13 16	0 13 16	1 7 -3											
4 64 93	2 43 -43	3 126 117	7 36 20	3 99 91	2 25 -7	3 0 13	1 30 -44	1 29 -29	2 20 -30											
H <sub>1</sub> L <sub>1</sub> =-9 0	3 67 -95	4 7 0	H <sub>1</sub> L <sub>1</sub> =0 2	4 6 -1	2 42 -41	4 0 -4	2 42 -32	2 75 78	H <sub>1</sub> L <sub>1</sub> =0 8											
2 11 -2	4 30 23	H <sub>1</sub> L <sub>1</sub> =11 1	0 731-753	6 72 66	4 40 -51	5 0 -18	3 57 49	3 20 -20	1 5 10											
3 39 44	5 57 53	1 15 -25	1 103-103	6 25 26	4 36 -27	6 2 1	4 19 14	4 35 38	H <sub>1</sub> L <sub>1</sub> =-1 8											
4 30 -35	6 39 42	2 22 -22	2 97 -88	7 32 15	H <sub>1</sub> L <sub>1</sub> =-4 4	H <sub>1</sub> L <sub>1</sub> =6 4	H <sub>1</sub> L <sub>1</sub> =-5 5	H <sub>1</sub> L <sub>1</sub> =10 7	0 24 23											
H <sub>1</sub> L <sub>1</sub> =-8 0	H <sub>1</sub> L <sub>1</sub> =-6 1	4 16 11	4 56 -40	1 98 -90	H <sub>1</sub> L <sub>1</sub> =-2 3	1 66 -17	1 0 -8	2 35 28	H <sub>1</sub> L <sub>1</sub> =2 8											
0 117 127	H <sub>1</sub> L <sub>1</sub> =-6 1	4 16 11	4 56 -40	1 98 -90	1 52 36	2 14 5	3 0 12	2 0 -46	H <sub>1</sub> L <sub>1</sub> =3 8											
1 44 38	1 107 -98	H <sub>1</sub> L <sub>1</sub> =17 1	5 13 13	2 41 37	2 43 30	H <sub>1</sub> L <sub>1</sub> =7 4	4 7 -9	3 14 -14	1 6 -8											
2 85 -82	2 23 -14	1 54 63	6 171-151	3 99 98	3 26 16	0 0 2	H <sub>1</sub> L <sub>1</sub> =-6 5	4 23 -29	H <sub>1</sub> L <sub>1</sub> =4 8											
3 0 13	3 46 -53	2 0 -3	7 23 -18	4 47 36	4 48 43	0 0 2	H <sub>1</sub> L <sub>1</sub> =-11 6	1 24 17	H <sub>1</sub> L <sub>1</sub> =6 8											
4 45 -42	4 29 -2	3 34 -33	8 18 -23	5 17 -9	6 17 9	2 13 -16	2 24 17	1 0 3	H <sub>1</sub> L <sub>1</sub> =-6 8											
5 34 -34	5 66 -62	H <sub>1</sub> L <sub>1</sub> =15 2	H <sub>1</sub> L <sub>1</sub> =1 2	6 29 -15	6 17 9	2 13 -16	2 24 17	1 0 3	H <sub>1</sub> L <sub>1</sub> =-6 8											
6 40 32	H <sub>1</sub> L <sub>1</sub> =-5 1	2 16 -17	0 445-461	7 50 -43	H <sub>1</sub> L <sub>1</sub> =5 4	H <sub>1</sub> L <sub>1</sub> =8 4	H <sub>1</sub> L <sub>1</sub> =-7 5	1 0 3	0 54 56											
H <sub>1</sub> L <sub>1</sub> =-7 0	1 0 7	H <sub>1</sub> L <sub>1</sub> =-14 2	1 68 -69	8 21 28	0 94 94	0 86 82	1 30 21	2 25 28	H <sub>1</sub> L <sub>1</sub> =7 8											
0 223-230	2 69 87	0 47 -41	2 38 30	H <sub>1</sub> L <sub>1</sub> =-3 3	1 52 37	1 0 9	2 8 -9	3 0 10	0 17 -27											
1 24 22	2 43 -43	3 22 -31	3 21 -31	4 1 45	2 5 1	3 0 -1	4 40 43	4 40 43	H <sub>1</sub> L <sub>1</sub> =8 8											
2 29 -30	4 2 0	2 2 0	4 38 24	2 72 53	3 14 12	H <sub>1</sub> L <sub>1</sub> =9 4	H <sub>1</sub> L <sub>1</sub> =-8 5	H <sub>1</sub> L <sub>1</sub> =12 0	0 15 8											
3 0 -7	H <sub>1</sub> L <sub>1</sub> =-4 1	H <sub>1</sub> L <sub>1</sub> =13 2	5 0 -3	3 98 91	4 16 -14	0 14 -20	1 21 -22	0 42 -47	1 0 -10											
4 19 18	1 57 -59	0 48 48	6 110 96	4 53 -38	5 35 -20	1 0 0	2 8 -10	1 0 7	2 15 18											
5 0 15	2 56 43	2 20 17	7 25 -17	5 0 4	6 29 30	2 39 44	3 118-118	2 17 -17	H <sub>1</sub> L <sub>1</sub> =9 8											
6 59 -65	1 80 94	4 15 19	6 15 12	6 36 -25	7 18 -6	H <sub>1</sub> L <sub>1</sub> =-6 5	5 3 0 4	0 4 -2	0 4 -2											
H <sub>1</sub> L <sub>1</sub> =-6 0	4 18 -16	H <sub>1</sub> L <sub>1</sub> =-17 2	H <sub>1</sub> L <sub>1</sub> =2 2	7 35 19	0 100 99	1 113-110	1 10 -8	1 10 -8	H <sub>1</sub> L <sub>1</sub> =1 8											
0 108-115	5 0 13	0 39 -49	0 127 141	8 22 9	1 36 -27	2 43 29	2 0 -4	H <sub>1</sub> L <sub>1</sub> =-13 6	0 98 -80											
1 73 -66	6 28 -24	2 40 -38	1 51 40	H <sub>1</sub> L <sub>1</sub> =-4 3	2 32 21	3 0 -8	3 118 120	0 33 42	1 33 -29											
2 33 20	7 24 -18	4 42 -55	2 120-111	1 53 41	3 0 -1	4 15 -12	4 28 36	H <sub>1</sub> L <sub>1</sub> =-14 6	n 8 6											
3 31 -19	H <sub>1</sub> L <sub>1</sub> =-3 1	H <sub>1</sub> L <sub>1</sub> =-13 2	3 25 -13	4 14 -11	5 18 -4	6 71 -67	3 26 20	0 13 -13	0 15 8											
4 12 7	1 126-128	1 14 21	4 100 -85	3 103 -98	5 18 -4	6 71 -67	3 26 20	0 13 -13	0 15 8											
5 37 25	2 63 -50	2 50 44	5 0 4	4 13 -7	6 37 34	7 14 -9	4 19 -18	2 4 -4	H <sub>1</sub> L <sub>1</sub> =1 6											
6 0 -22	3 65 -49	3 24 22	6 39 24	H <sub>1</sub> L <sub>1</sub> =-5 3	H <sub>1</sub> L <sub>1</sub> =-7 4	H <sub>1</sub> L <sub>1</sub> =-11 5	H <sub>1</sub> L <sub>1</sub> =-11 5	5 1 6	0 173 175											
7 19 -17	4 64 61	4 28 24	7 17 8	1 16 1	0 161-170	1 52 44	1 65 62	1 37 33	1 37 33											
H <sub>1</sub> L <sub>1</sub> =-5 0	5 2 4	5 28 -44	8 14 -6	2 75 -69	1 53 -50	2 97 87	2 27 25	1 37 33	1 37 33											
0 103 100	6 20 20	H <sub>1</sub> L <sub>1</sub> =10 2	H <sub>1</sub> L <sub>1</sub> =3 2	3 4 6	2 36 25	3 101-93	3 36 37	2 8 14	0 2 2											
1 55 -43	7 38 -40	1 17 18	0 30 -14	4 18 19	3 14 -17	4 31 -26	4 8 -8	5 0 2	5 0 2											
2 48 -52	8 0 1	2 110-110	1 61 47	5 0 3	4 19 15	5 57 46	H <sub>1</sub> L <sub>1</sub> =1 5	4 20 11	H <sub>1</sub> L <sub>1</sub> =2 6											
3 23 -13	H <sub>1</sub> L <sub>1</sub> =-2 1	3 0 13	2 195 196	6 34 24	5 46 42	6 29 -16	1 48 30	H <sub>1</sub> L <sub>1</sub> =2 6	0 35 -41											
4 59 -61	1 80 94	4 65 -40	3 25 12	H <sub>1</sub> L <sub>1</sub> =-6 3	6 52 -53	7 18 -6	2 28 -24	0 14 -14	1 14 -14											
5 28 15	2 128-122	H <sub>1</sub> L <sub>1</sub> =-9 4	4 121 104	H <sub>1</sub> L <sub>1</sub> =-9 4	1 113 101	H <sub>1</sub> L <sub>1</sub> =3 3	3 16 14	2 0 8	0 37 37											
H <sub>1</sub> L <sub>1</sub> =-4 0	3 202-200	0 29 21	5 25 -28	2 26 -16	0 34 20	1 51 -43	4 5 13	2 0 8	1 0 -12											
0 103 107	4 27 -17	1 41 -34	6 24 4	3 33 26	1 31 17	2 50 -53	H <sub>1</sub> L <sub>1</sub> =2 5	3 0 -3	3 0 -3											
1 70 63	5 0 5	2 81 -69	7 0 -3	4 16 11	2 38 -44	3 82 73	1 42 -36	4 4 -8	4 4 -8											
2 31 27	6 41 37	5 55 -58	8 19 29	5 78 69	3 23 -28	4 21 -15	2 40 -34	H <sub>1</sub> L <sub>1</sub> =3 6	0 37 37											
3 40 40	7 39 31	4 63 -48	9 0 2	6 0 10	4 15 -5	5 0 4	3 49 32	1 0 12	1 0 12											
4 26 17	H <sub>1</sub> L <sub>1</sub> =-1 1	5 25 23	0 87 -83	7 25 7	5 13 -11	6 23 18	4 19 10	3 5 2	2 47 42											
5 48 -35	1 265-258	H <sub>1</sub> L <sub>1</sub> =-8 2	1 24 14	H <sub>1</sub> L <sub>1</sub> =-7 3	H <sub>1</sub> L <sub>1</sub> =-9 4	7 25 -21	H <sub>1</sub> L <sub>1</sub> =3 5	2 0 8	3 0 8											
H <sub>1</sub> L <sub>1</sub> =-6 0	2 47 48	0 81 -65	2 51 -35	1 60 -54	0 29 -30	H <sub>1</sub> L <sub>1</sub> =4 3	1 0 8	4 4 6	4 4 6											
1 93 76	3 88 56	1 48 -42	3 27 20	2 47 36	1 46 39	1 17 25	2 42 47	3 54 -55	H <sub>1</sub> L <sub>1</sub> =0 -3											
2 224-221	H <sub>1</sub> L <sub>1</sub> =0 1	3 0 7	5 24 -11	4 9 -4	3 44 44	3 47 43	4 7 5	1 0 -2	1 0 -2											
3 0 -1	1 79 79	4 43 26	6 21 -25	5 34 -21	4 67 -57	4 35 36	H <sub>1</sub> L <sub>1</sub> =4 5	1 0 2	2 39 -36											
4 88 -92	2 113 102	5 31 30	7 13 9	6 45 -39	H <sub>1</sub> L <sub>1</sub> =-10 4	5 0 -5	1 28 -22	3 0 -2	3 0 -2											
5 48 -33	3 44 27	6 29 -15	7 19 14	8 19 -14	0 0 -12	6 22 21	2 14 14	3 0 2	4 19 -28											
H <sub>1</sub> L <sub>1</sub> =-2 0	4 64 -52	0 111 -114	H <sub>1</sub> L <sub>1</sub> =8 3	H <sub>1</sub> L <sub>1</sub> =-8 3	7 21 13	7 21 13	4 19 -28	4 19 -28	H <sub>1</sub> L <sub>1</sub> =5 6											
0 212-221	5 56 38	0 253 272	1 59 -52	1 47 38	2 97 78	H <sub>1</sub> L <sub>1</sub> =5 3	4 16 -22	H <sub>1</sub> L <sub>1</sub> =5 6	0 11 15											
1 50 -34	6 189-106	1 36 26	2 23 25	2 26 18	3 0 6	1 32 28	H <sub>1</sub> L <sub>1</sub> =5 5	0 11 15	1 0 -9											
2 251 254	7 0 -3	2 4 9	3 25 -19	3 97 87	4 45 33	2 0 5	2 11 -19	2 7 -1	2 7 -1											
3 60 -57	8 24 19	3 29 21	4 35 32	4 26 -23	H <sub>1</sub> L <sub>1</sub> =11 4	3 66 -52	3 37 32	H <sub>1</sub> L <sub>1</sub> =6 6	0 24 31											
4 130 141	H <sub>1</sub> L <sub>1</sub> =1 1	4 27 -18	5 38 26	5 0 0	0 0 -5	4 18 -4	2 19 -17	0 37 -35	0 24 31											
5 38 28	1 268 257	5 43 -37	6 112 123	7 14 23	1 0 -15	5 0 -13	2 11 -15	0 24 31	0 24 31											
6 43 -28	2 16 1	3 26 -20	8 12 23	H <sub>1</sub> L <sub>1</sub> =-9 3	3 0 -19	H <sub>1</sub> L <sub>1</sub> =6 3	1 30 -31	H <sub>1</sub> L <sub>1</sub> =21 25	H <sub>1</sub> L <sub>1</sub> =7 6											
7 0 2	3 10 3	0 28 -11	2 31 -15	1 4 -13	4 33 -43	1 32 -27	H <sub>1</sub> L <sub>1</sub> =12 5	H <sub>1</sub> L <sub>1</sub> =8 6	H <sub>1</sub> L <sub>1</sub> =8 6											
8 38 18	4 0 2	1 77 70	3 8 -7	2 21 -20	H <sub>1</sub> L <sub>1</sub> =12 4	2 37 36	2 19 -17	0 37 -35	0 37 -35											
H <sub>1</sub> L <sub>1</sub> =-1 0	5 114 109	2 40 -24	4 18 -20	3 180-199	0 50 53	3 10 -5	H <sub>1</sub> L <sub>1</sub> =-13 5	H <sub>1</sub> L <sub>1</sub> =0 7	0 7 7											
0 272-280	6 54 46	3 31 16	5 27 12	4 28 -23	1 0 -9	4 0 -10	4 9 9	1 50 -48	H <sub>1</sub> L <sub>1</sub> =-1 7											
1 119-143	7 40 2	4 12 9	6 36 36	5 21 -14	2 35 28	5 0 -2	H <sub>1</sub> L <sub>1</sub> =-14 5	H <sub>1</sub> L <sub>1</sub> =1 7	1 25 34											
2 29 -37	H <sub>1</sub> L <sub>1</sub> =2 1	1 47 -63	5 0 -17	H <sub>1</sub> L <sub>1</sub> =7 2	H <sub>1</sub> L <sub>1</sub> =10 3	6 23 -24	3 37 48	1 25 34	1 25 34											
3 0 10	1 47 -63	5 0 -17	H <sub>1</sub>																	

The values for the observed intensities ranged from 1 to 10000. Out of 1034 observed reflexions 724 were independent. The intensities were corrected for Lorentz and polarization factors to obtain relative values of  $|F(hkl)|^2$  and were converted to the absolute values by Wilson's (1942) statistical method.

### Structure determination

Since the ultraviolet absorption spectrum of the crystal shows a characteristic band associated with the hydrogen bonding along the  $b$  axis (Tanaka & Tanaka, 1967) and cleavage occurs easily parallel to the (001) and (100) planes, it is expected that the hydrogen bonds will be along the  $b$  axis, and it is also conceivable that molecular plane and the hydrogen bond network form a planar sheet in the crystal.

The Patterson function projected along the  $b$  axis is shown in Fig. 1. The arrangement of peaks in Fig. 1 at once indicated that the molecules were nearly parallel to the (001) plane. The angle of tilt of the molecular

plane was estimated to be about  $5^\circ$  to the (001) plane, from the inclination of the row of peaks. The minimum function method was applied, using several sets of origins which were sought from the Harker sections at  $V=0.5$ . The result was a much clearer picture, and the atomic coordinates for the molecular skeleton were obtained immediately. Several cycles of least-squares refinement with block-diagonal and anisotropic temperature factor approximations were carried out and the final  $R$  value was reduced to 0.149. The final atomic coordinates are listed in Table 1 and the  $F_o$  and  $F_c$  values are shown in Table 2. At this stage of the refinement the electron density projection on the (001) plane was calculated, which is shown in Fig. 2. The difference-Fourier synthesis is also shown in Fig. 3.

The calculations were carried out at the Takeda Chemical Industries at the initial stage and at the Computation Center of the University of Tokyo in the final refinement. The least-squares program written by Dr Ashida in the *UNICS* system was employed.

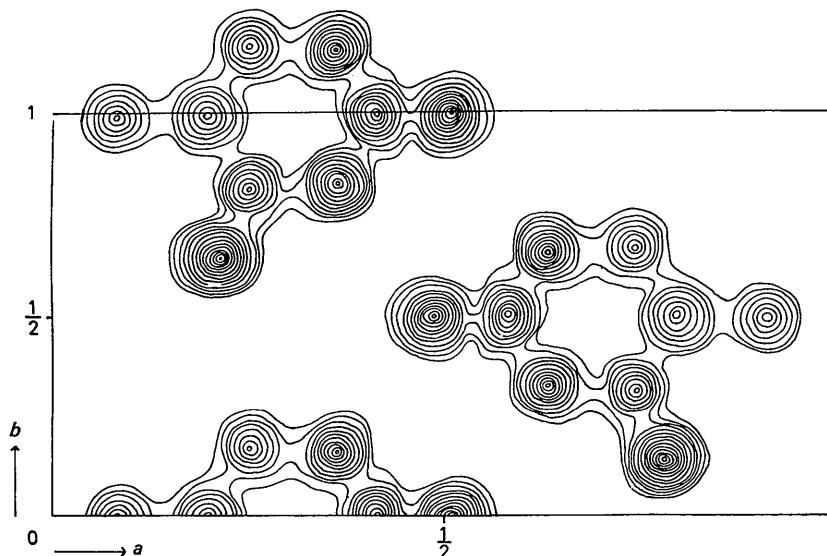


Fig. 2. Final Fourier synthesis along the  $c$  axis. Contours at equal intervals, beginning with the zero contour.

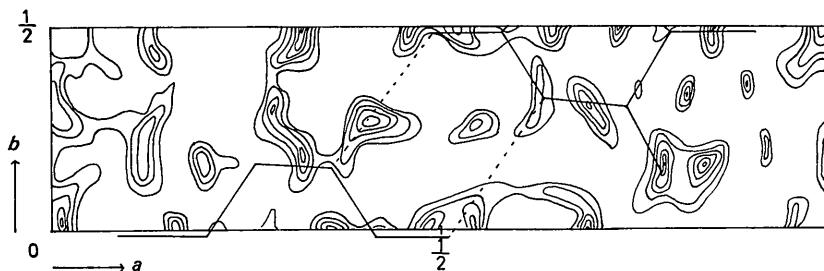


Fig. 3. The  $(F_o - F_c)$  electron density evaluated at the level  $(x, y, \frac{1}{2})$ . Contours are drawn at the interval of one tenth of that of the Fourier synthesis (Fig. 2). Lines indicate the molecular skeleton. Dashed lines represent hydrogen bonds.

### Discussion of the structure

#### The molecular arrangement

The projection of the structure upon the plane (100) is illustrated in Fig.4. The plane of the molecule is nearly parallel to the plane (001) and it is defined by the equation

$$0.0682x - 0.0566y + 0.944z = 4.922.$$

This plane is inclined at 3.3 degrees and 4.1 degrees to the  $a$  and  $b$  axes, respectively. It is seen that the two-dimensional network of hydrogen bonding is developed parallel to the plane (001). The bond distances and angles together with the intermolecular hydrogen bond distances are compared with the results of an investigation of thymine monohydrate by Gerdil (1961) in Figs.5 and 6.

In the present crystal the twofold screw axis is at  $(\frac{1}{2}, y, \pm \frac{1}{4})$  and  $(0, y, \pm \frac{1}{4})$ . By the symmetry operation of the twofold screw axis molecule  $M$  is transformed into  $M'$  and  $M''$ , and these molecules are connected by the two hydrogen bonds. These hydrogen bonds are not equal in length, while in the monohydrate crystal the hydrogen bond distances are equivalent.

The plane of molecule  $M$  coincides with neither the molecular plane of  $M'$  nor the plane of the hydrogen bonds. In the case of the thymine monohydrate crystal, the molecule  $M$  is related to molecules  $M'$  and  $M''$  by an inversion symmetry and the molecular plane of  $M$  is coplanar both with the  $M'$  and  $M''$  planes and the planes of the hydrogen bonds. It is remarkable that the shortest hydrogen bond distance is observed in the anhydrate crystal in the non-planar hydrogen bonding system, in which the hydrogen atom will be out of the line connecting the nitrogen and oxygen atoms.

This result indicates that the covalent resonance structure is important in the shortest hydrogen bond, since if the ionic structure is the more prevalent, the hydrogen atom should be on the line connecting the nitrogen and oxygen atoms (Coulson, 1961; Coulson & Danielson, 1954).

The stacking of molecules in the monohydrate crystal is compared with that of molecules in the anhydrate

crystal. It is found that in the monohydrate crystal (Fig.7) the interplanar spacing is 3.4 Å and the molecules form an infinite chain and are superimposed by a simple translation. In the anhydrate crystal shown in Fig.8, the overlapping of the different molecules in adjacent layers is only slight. The planes of neigh-

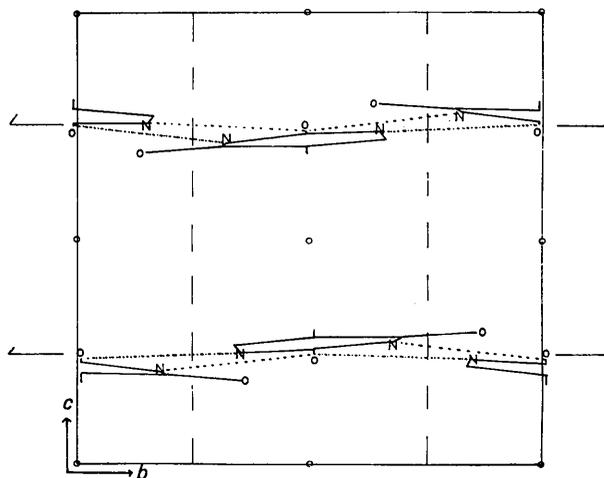


Fig.4. The structure viewed along the  $a$  axis. Four molecules in a unit cell are shown.

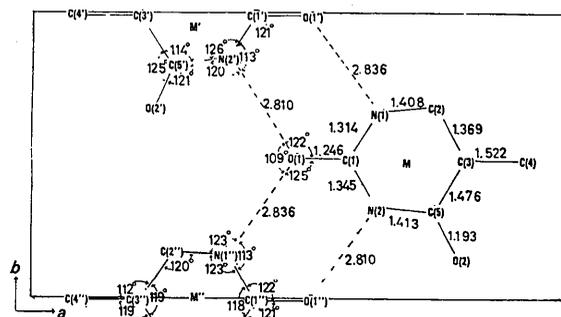


Fig.5. Bond distances and bond angles of thymine in the anhydrate crystal projected onto the (001) plane.

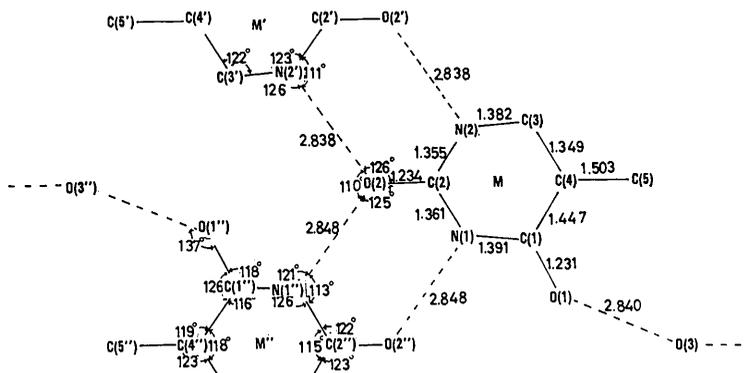


Fig.6. Bond distances and bond angles of thymine in the monohydrate crystal taken from the results of Gerdil (1961).

bouring molecules in a layer are inclined at an angle of  $6.60^\circ$  to each other. The average interplanar spacing between adjacent layers is  $3.36 \text{ \AA}$ .

#### The thymine molecule

The intramolecular bond lengths and angles are listed in Table 3. The nine atoms in the thymine molecules are nearly coplanar; the average deviation of the six ring atoms from the plane is  $0.010 \text{ \AA}$  with a maximum deviation of  $0.018 \text{ \AA}$  for the C(2) atom. The departure from this plane of the three atoms attached to the ring ( $0.045 \text{ \AA}$ ) is the maximum value. The average standard deviation for bond lengths is  $0.012 \text{ \AA}$ .

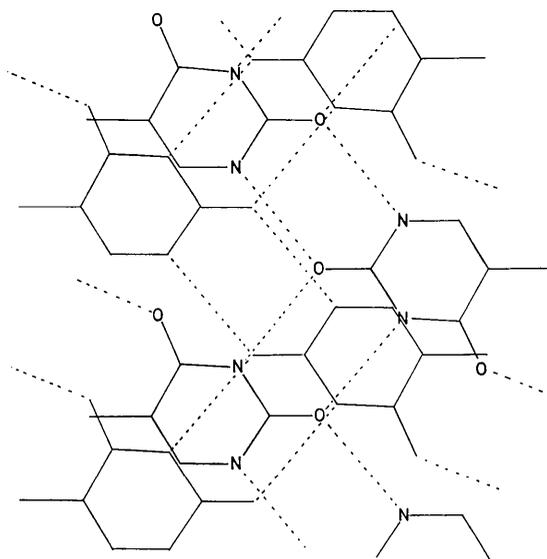


Fig. 7. The stacking of molecules in the thymine monohydrate crystal viewed perpendicular to the molecular planes. Two adjacent layers are shown. The positions of nitrogen and oxygen atoms are indicated in one layer but only the molecular skeleton is shown in the other layer.

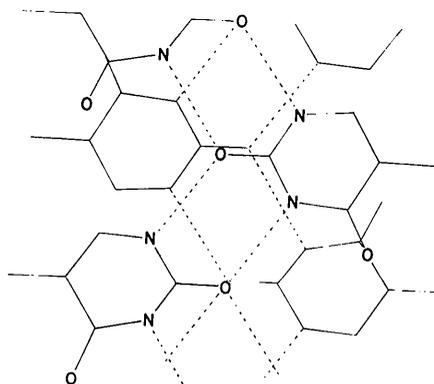


Fig. 8. The stacking of molecules in the thymine anhydrate crystal viewed perpendicular to the plane (001). Two adjacent layers are shown; one indicates the positions of the nitrogen and oxygen atoms, the other only the molecular skeleton.

Table 3. Intramolecular bond distances and bond angles

O(1)–C(1)	1.246 ± 0.015 Å	O(1)–C(1)–N(1)	122 ± 1°
C(1)–N(1)	1.314 0.016	O(1)–C(1)–N(2)	121
N(1)–C(2)	1.408 0.017	N(1)–C(1)–N(2)	118
C(2)–C(3)	1.369 0.016	C(1)–N(1)–C(2)	123
C(3)–C(4)	1.522 0.018	N(1)–C(2)–C(3)	120
C(3)–C(5)	1.476 0.017	C(2)–C(3)–C(4)	112
C(5)–O(2)	1.193 0.014	C(2)–C(3)–C(5)	119
C(5)–N(2)	1.413 0.015	C(4)–C(3)–C(5)	119
N(2)–C(1)	1.345 0.016	C(3)–C(5)–N(2)	114
O(1)–N(1)	2.810 0.022	C(3)–C(5)–O(2)	125
N(1)–O(1)	2.836 0.022	O(2)–C(5)–N(2)	121
		C(5)–N(2)–C(1)	126
		C(1)–O(1)–N(2)	122
		C(1)–O(1)–N(1)	125
		N(2)–O(1)–N(1)	109
		O(1)–N(1'')–C(1'')	113
		O(1)–N(1'')–C(2'')	123
		O(1)–N(2')–C(1')	113
		O(1)–N(2')–C(5')	120

#### Comparison with crystals of other thymine and uracil derivatives

The hydrogen bond distances  $N(2) \cdots O'(1)$ , in the anhydrate crystal are certainly shorter than other hydrogen bonding distances, and this may have some influence on the intramolecular bond lengths. Comparison of bond lengths between the anhydrate and the monohydrate crystals shows that the bonds  $N(1)–C(1)$  and  $N(2)–C(1)$  of the anhydrate are shorter than  $N(2)–C(2)$  and  $N(1)–C(9)$  of the monohydrate while  $C(1)–O(1)$  of the former is longer than  $C(2)–O(2)$  of the latter. This result is explained if the resonance structure of type (III) in Fig. 9 contributes to the hydrogen bond.

The structure (I) is the usual covalent formula, (II) is the charge-transferred structure and (III) is the enolic structure, which is obtained by a further intramolecular charge migration in structure (II). The resonance structure (III) will be more stable than (II). If the resonance structure (III) is much involved in the hydrogen bond, the  $N(1)–C(1)$  and  $N(2)–C(1)$  distances will become shorter and the  $C(1)–O(1)$  bond length will become longer. Thus the carbonyl bond length will be influenced by the hydrogen bond formation and this can be seen in other systems.

The bond length  $C(5)–O(2)$  is  $1.193 \text{ \AA}$ , which is apparently shorter than  $C(1)–O(1)$  ( $1.246 \text{ \AA}$ ). In the monohydrate crystal, the  $C(1)–O(1)$  bond distance is  $1.231 \text{ \AA}$ , where  $O(1)$  is connected with the hydrogen atom of the water. In the 1-methylthymine crystal analysed by Hoogsteen (1963), one of the two carbonyl groups is hydrogen bonded, and this  $C–O$  bond length is longer than the other  $C–O$  bond which is free.

The hydrogen bond length in 5-ethyl-6-methyluracil, which was studied by Reeke & Marsh (1966), is as short as  $2.78 \text{ \AA}$  between the  $N(1)–O(7)$  atoms, and it is interesting that in this case also the two molecules are not coplanar and the hydrogen atom is not on the line connecting the nitrogen and oxygen atoms.

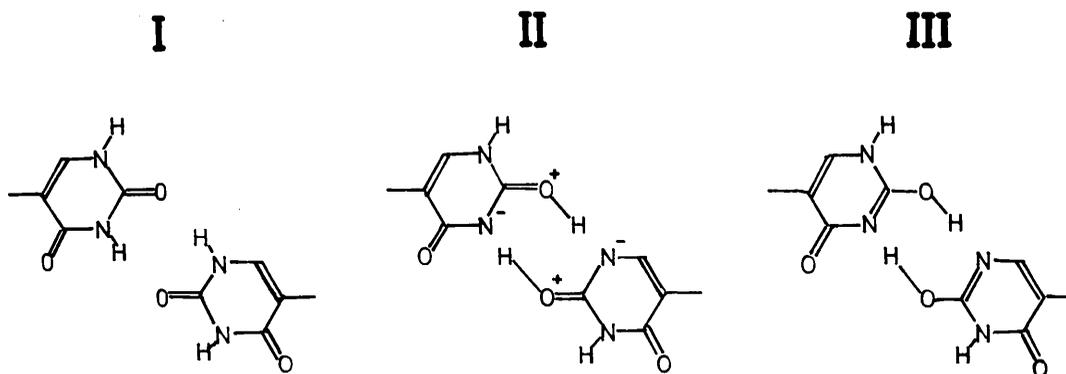


Fig.9. Important resonance structures of thymine in the crystal.

### The temperature factors

Thermal motion parameters,  $U_{ij}$ , are tabulated in Table 4 and illustrated in Fig. 10. The terminal methyl group has the largest thermal vibration, along the  $c$  axis, and this might be expected since the methyl group is attached to the benzene ring by a single bond. The O(1) atom shows a larger vibration than the O(2) atom and it is interesting that the O(1) atom is hydrogen bonded with the N(1) and N(2) atoms of molecules  $M''$  and  $M'$ , shown in Fig. 5, while the O(2) atom is free. The ellipsoids of the two nitrogen atoms are almost of the same size and they have large components in the plane of the molecule.

Table 4. The principal axis of thermal motion  $U_i$  and direction cosines  $q_i$  relative to the three crystallographic axes

Atom axis $i$	$U_i$	$q_i^a$	$q_i^b$	$q_i^c$
C(1)	1	0.118	0.968	-0.078
	2	0.170	-0.220	-0.727
	3	0.210	-0.124	0.682
C(2)	1	0.102	-0.703	0.060
	2	0.205	-0.248	-0.955
	3	0.246	0.667	-0.290
C(3)	1	0.150	-0.726	-0.571
	2	0.194	0.411	0.085
	3	0.204	0.551	-0.817
C(4)	1	0.166	-0.844	0.200
	2	0.247	-0.349	-0.909
	3	0.295	0.407	-0.365
C(5)	1	0.144	-0.406	0.765
	2	0.175	-0.826	-0.541
	3	0.195	0.390	-0.350
N(1)	1	0.149	0.124	0.482
	2	0.190	0.562	0.686
	3	0.226	0.818	-0.545
N(2)	1	0.154	0.126	0.337
	2	0.194	0.635	0.695
	3	0.210	-0.767	-0.635

Atoms axis $i$	$U_i$	$q_i^a$	$q_i^b$	$q_i^c$
O(1)	1	0.151	-0.218	0.798
	2	0.187	0.540	0.578
	3	0.262	0.813	-0.171
O(2)	1	0.115	-0.455	0.851
	2	0.177	-0.853	-0.501
	3	0.198	0.257	-0.155

It is known that the thymine dimer is formed in aqueous solution at freezing point by irradiation with ultraviolet light. In this situation thymine crystals will have water of crystallization. The structure of the thymine dimer has been discussed from several viewpoints (Wulff & Frankel, 1961), and it is suggested that the cross-linkage takes place at the C(2) and C(3) positions,

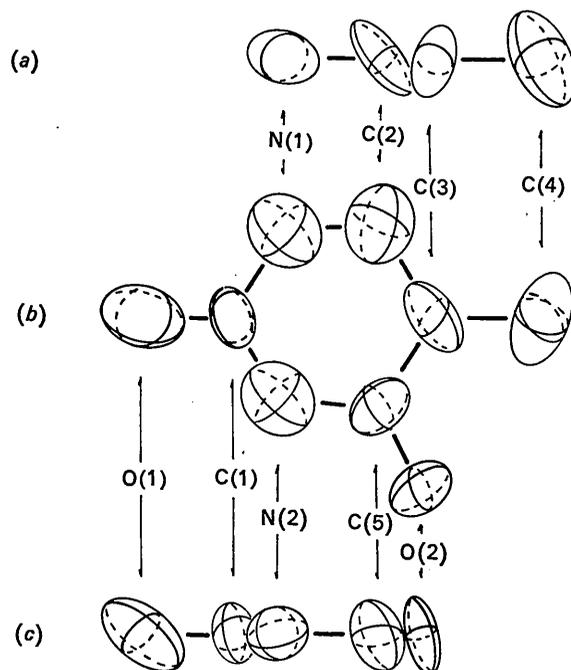


Fig.10. The ellipsoids defined by the principal axes of thermal motion, viewed perpendicular (b) and parallel (a and c) to the molecular plane.

using the anhydrate notation. If the photochemical changes occur in the solid state, it should be much easier for hydrate crystal rather than for the anhydrate. In the former crystal only the sliding of molecules will be required for the dimer formation, and therefore the geometrical conditions favour the monohydrate crystal.

The authors are grateful to Takeda Chemical Industries, Ltd. for making a computer available, and indebted to Dr M. Nishikawa and Mr K. Kamiya for the calculations. We are also indebted to Professor T. Ashida of Osaka University and Dr A. Furusaki of Kwansai Gakuin University for their kind help in the calculations.

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## The Structure of 3,5-Dichloroanthranilic Acid\*

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The crystals of 3,5-dichloroanthranilic acid,  $\text{NH}_2\text{Cl}_2\text{C}_6\text{H}_2\text{COOH}$ , are monoclinic, space group  $P2_1/a$ , with  $a=12.49$ ,  $b=17.02$ ,  $c=3.80$  Å;  $\beta=92.7^\circ$ ;  $\rho_o$ ,  $1.700$  g.cm $^{-3}$ ;  $\rho_c$  for  $Z=4$ ,  $1.705$  g.cm $^{-3}$ ;  $\mu$  for Cu  $K\alpha$ ,  $70.4$  cm $^{-1}$ .

The effect of intramolecular overcrowding between the carboxylic group and the amino group is to cause the exocyclic carbon atom and the nitrogen atom to be displaced from the aromatic plane in opposite directions by  $0.063$  Å and  $0.045$  Å respectively. One of the chlorine atoms is displaced from the aromatic plane by  $0.078$  Å owing to intermolecular interactions.

### Introduction

The structure of 3,5-dichloroanthranilic acid is interesting in the sense that the molecule shows distortions from planarity which can be accounted for as being a result of the presence of both intermolecular and intramolecular overcrowding. The present study is a continuation of similar structural studies of simple aromatic compounds made in this laboratory.

The crystals grown from acetic acid are needles elongated along the  $c$  axis; they are monoclinic, space group  $P2_1/a$ , with

$$a=12.49, b=17.02, c=3.80 \text{ \AA}; \beta=92.7^\circ; \\ \rho_o, 1.700 \text{ g.cm}^{-3}; \rho_c \text{ for } Z=4, 1.705 \text{ g.cm}^{-3}; \\ \mu \text{ for Cu } K\alpha, 70.4 \text{ cm}^{-1}.$$

### Experimental

The axial lengths were determined from equatorial Weissenberg photographs.

Reflexions of the type  $hk0$  to  $hk3$  were obtained from equi-inclination Weissenberg photographs by the use of Cu radiation and a crystal of roughly  $0.3 \times 0.6$  mm $^2$  cross-section. The visually estimated intensities from

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extended spots were corrected for the Lorentz-polarization-Tunell factor as well as for the effect of spot extension; absorption was neglected. In all, 506 reflexions (including 5 unobserved reflexions) out of nearly 1374 possible for these layers were used for refinement;  $0,6,0$  and  $0,12,0$  appeared to be Renninger reflexions and were left out. The scaling of different layers was done with the help of common reflexions in zero-layer Weissenberg photographs along the other axes.

### Determination and refinement of the structure

The structure was solved with the help of Patterson projections and refined to an  $R$  value of 12.2% using individual isotropic temperature factors; the scale factors used at this stage were 1.00, 1.03, 1.07 and 0.89 for the zero to third layers respectively and the individual isotropic temperature factors were all within the range  $1.8$  Å $^2$  to  $2.2$  Å $^2$ . Temperature factors of the form

$$\exp[-(a_{11}h^2 + a_{22}k^2 + a_{33}l^2 + 2a_{12}hk + 2a_{13}hl + 2a_{23}kl)]$$

were then introduced and the  $a_{ij}$  were refined (Rollett & Davis, 1955) along with the atomic parameters, to an  $R$  value of 10.5%. The final atomic parameters are given in Table 1 and  $F_o$  and  $F_c$  in Table 2. Owing probably to absorption effects and imperfect scaling, the thermal parameters did not seem reliable and have not been given.

\* Communication No. 2001 from the National Chemical Laboratory, Poona, India.