

Temperature parameters are given in Table 4. Calculations of the thermal ellipsoids yielded very little of value. No clear evidence was to be seen of any rigid-body motions, and the only general feature of note was the larger amplitudes of vibration of the hydroxyl and nitro groups.

The observed and calculated structure amplitudes, the calculated phase angles and the e.s.d.'s of the observed amplitudes are listed in Table 5.

The authors wish to express their gratitude to Dr H. Hofer and Mrs Susan Arnaudon for assistance in preparing the diagrams.

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The 5-Hydroxyl Configuration in Dialuric Acid Monohydrate by Neutron Crystal Structure Determination

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(Received 15 May 1968 and in revised form 29 October 1968)

The crystal structure of dialuric acid monohydrate (5,6-dihydroxyuracil) has been reinvestigated with three-dimensional neutron diffraction data, in order to obtain more accurate hydrogen atom positions than in Bolton's X-ray determination. The crystal data of Bolton (*Acta Cryst.* (1965) **19**, 1051) were assumed, *i.e.* $a=12.714$, $b=3.676$, $c=12.949$ Å, $\beta=94^\circ 24'$, space group $P2_1/n$, with four formula units, $C_4H_4O_4N_2 \cdot H_2O$, in the unit cell. With 871 neutron data above background, least-squares refinement of positional and anisotropic thermal parameters for all atoms gave a final R index of 0.05. Molecular association in this crystal structure is dominated by conventional hydrogen bonds (two NH---OC bonds and three hydrogen bonds involving the water molecule) and van der Waals interactions within stacks of parallel, almost flat, dialuric acid molecules. Averaged over time, the O—H bond of the 5-hydroxyl group is found to be restricted to a range of about 50° of the full rotation about the C—O bond. In its mean position, this bond is twisted 67° from the configuration of molecular coplanarity in which the hydrogen atom is nearest the 4-position of the pyrimidine ring. There are weak hydrogen bonding interactions of the 5-hydroxyl group throughout the observed range of O—H twist, with no position seeming to be particularly favourable. For the non-hydrogen atoms, the greatest discrepancy between X-ray and neutron bond lengths is 0.014 Å for N(1)—C(6) for which the estimated standard deviation is 0.005 Å.

Introduction

An X-ray crystal structure determination of dialuric acid monohydrate (5,6-dihydroxyuracil, I) was first

reported by Alexander & Pitman (1956) for the structure in projection. Bolton (1965), using three-dimensional X-ray intensity data, confirmed the earlier work and reported the location of the imine hydrogen atoms.

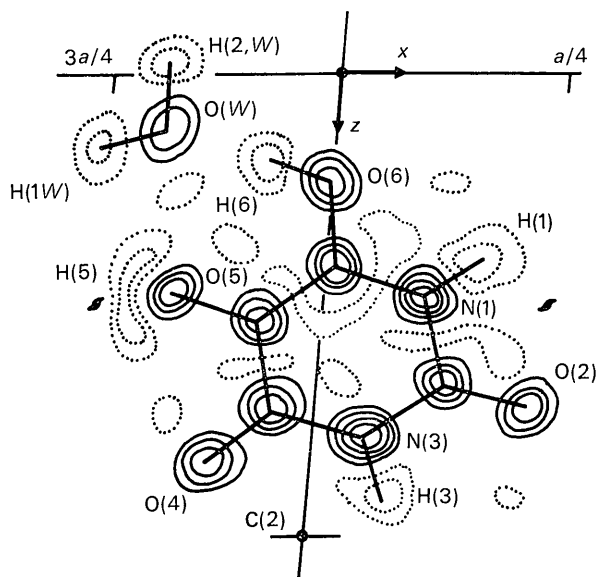
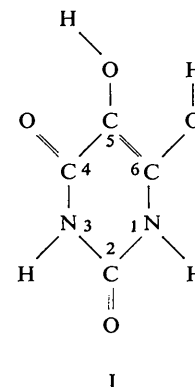


Fig. 1. Fourier synthesis projection of neutron scattering density, down *b*. Contours are on an arbitrary scale with negative contours dotted.

The remaining hydrogen atoms were not precisely determined. For atoms H(5) and H(2, *W*),* only tenta-



tive positions were assigned on the basis of difference

* The atom labelling in this paper is the same as that of Bolton (1965), except for the water molecule atoms O(*W*), H(1, *W*), H(2, *W*), which Bolton labelled O(7), H(7), H(8), respectively.

Table 1. *Atomic parameters with their e.s.d.'s*

The positional parameters *x*, $\sigma(x)$ etc. are expressed as fractions of the lattice translations. The thermal parameters are defined by the expression

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

The atoms listed here correspond to those in Table 1 of Bolton (1965).

	<i>x</i>	<i>y</i>	<i>z</i>	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
	$\sigma(x)$	$\sigma(y)$	$\sigma(z)$	$\sigma(\beta_{11})$	$\sigma(\beta_{22})$	$\sigma(\beta_{33})$	$\sigma(\beta_{12})$	$\sigma(\beta_{13})$	$\sigma(\beta_{23})$
N(1)	0.10945 0.00015	0.4548 0.0005	0.24209 0.00016	0.00228 0.00013	0.0511 0.0013	0.00225 0.00010	-0.0008 0.0003	0.00052 0.00009	0.0008 0.0003
H(1)	0.16791 0.00049	0.5424 0.0017	0.19942 0.00049	0.00366 0.00038	0.0801 0.0047	0.00399 0.00036	0.0015 0.0010	0.00134 0.00030	0.0034 0.0009
C(2)	0.13869 0.00020	0.2968 0.0006	0.33435 0.00019	0.00174 0.00014	0.0424 0.0016	0.00215 0.00014	0.0006 0.0004	0.00032 0.00011	-0.0006 0.0003
O(2)	0.23098 0.00026	0.2394 0.0009	0.36440 0.00026	0.00189 0.00019	0.0690 0.0025	0.00275 0.00018	0.0025 0.0005	0.00025 0.00014	-0.0013 0.0005
N(3)	0.05925 0.00014	0.2030 0.0005	0.39117 0.00014	0.00198 0.00011	0.0469 0.0012	0.00195 0.00012	0.0006 0.0003	0.00036 0.00008	0.0011 0.0003
H(3)	0.07997 0.00043	0.0744 0.0015	0.46125 0.00043	0.00322 0.00033	0.0694 0.0039	0.00325 0.00033	0.0013 0.0008	0.00039 0.00026	0.0044 0.0009
C(4)	-0.04612 0.00019	0.2625 0.0006	0.36335 0.00019	0.00196 0.00016	0.0358 0.0016	0.00182 0.00014	0.0009 0.0003	0.00039 0.00011	0.0009 0.0003
O(4)	-0.11178 0.00026	0.1665 0.0009	0.42273 0.00026	0.00236 0.00019	0.0612 0.0024	0.00289 0.00018	0.0009 0.0005	0.00100 0.00014	0.0050 0.0005
C(5)	-0.07194 0.00020	0.4287 0.0006	0.26560 0.00019	0.00197 0.00015	0.0363 0.0015	0.00214 0.00014	-0.0004 0.0003	0.00011 0.00011	0.0014 0.0003
O(5)	-0.17328 0.00030	0.5081 0.0009	0.23329 0.00029	0.00291 0.00021	0.0585 0.0024	0.00358 0.00020	0.0021 0.0006	-0.00029 0.00016	0.0031 0.0005
H(5)	-0.21470 0.00089	0.3053 0.0026	0.21840 0.00124	0.00731 0.00074	0.0850 0.0069	0.02115 0.00159	0.0011 0.0017	-0.00800 0.00093	-0.0058 0.0025
C(6)	0.00672 0.00021	0.5235 0.0006	0.20694 0.00018	0.00269 0.00016	0.0361 0.0015	0.00162 0.00014	-0.0007 0.0004	0.00037 0.00011	0.0009 0.0003
O(6)	-0.00345 0.00031	0.6841 0.0010	0.11734 0.00027	0.00394 0.00026	0.0662 0.0025	0.00253 0.00020	-0.0011 0.0006	0.00042 0.00017	0.0058 0.0005
H(6)	-0.07781 0.00054	0.7632 0.0017	0.09436 0.00048	0.00502 0.00048	0.0791 0.0048	0.00372 0.00037	0.0006 0.0011	-0.00071 0.00033	0.0024 0.0009
O(<i>W</i>)	-0.31514 0.00046	0.4551 0.0016	0.44486 0.00045	0.00573 0.00040	0.1337 0.0050	0.00571 0.00036	0.0072 0.0011	-0.00280 0.00028	-0.0186 0.0011
H(1, <i>W</i>)	-0.25194 0.00075	0.3492 0.0023	0.42966 0.00065	0.00644 0.00065	0.1070 0.0071	0.00612 0.00051	0.0028 0.0016	-0.00111 0.00047	-0.0051 0.0014
H(2, <i>W</i>)	-0.30120 0.00078	0.5751 0.0025	0.50940 0.00071	0.00896 0.00074	0.1264 0.0076	0.00488 0.00051	0.0023 0.0017	-0.00119 0.00048	-0.0122 0.0016

1972 THE 5-HYDROXYL CONFIGURATION IN DIALURIC ACID MONOHYDRATE

Table 2. Observed and calculated structure factors for dialuric acid monohydrate
Columns are: *l* index, 100|F_{obs}|, 100F_{calc}.

K=0 H=0	4 1304 1324	-4 132 126	-4 344 527	-11 42 25	-7 220 251	-3 430 61	13 145 168	6 430 47	2 485 483
9 843 1053	5 1334 231	-5 134 134	-5 434 533	-10 84 613	-7 343 333	-7 343 333	7 124 122	7 124 122	3 238 238
4 307 479	6 814 807	-1 350 83	-1 353 295	-9 499 476	-4 648 636	-1 430 68	-13 144 340	6 276 251	K=1 H=1
4 747 732	7 337 332	0 223 52	0 223 225	-9 1309 1319	-4 410 630	0 91 73	-12 430 26	K=1 H=1	-7 333 355
8 1066 965	8 174 184	1 185 196	1 84 75	-6 811 833	-4 410 833	1 656 653	-11 139 140	-13 271 282	-6 422 248
17 902 843	9 490 470	2 340 340	2 340 340	-5 101 101	-5 101 101	2 236 236	65 103	-12 109 113	-4 333 483
19 132 97	10 64 80	3 43 43	3 34 33	-6 148 144	-7 447 472	3 326 305	-11 42 83	-11 162 184	-3 375 360
14 138 97	11 338 347	4 76 107	4 36 53	-3 251 263	-1 260 275	4 216 223	-8 107 86	-10 511 519	-2 400 425
K=0 H=1	12 319 315	5 284 312	5 163 161	-2 177 176	1 164 165	5 136 133	-7 410 31	-9 274 256	-1 349 296
-15 139 15	13 430 85	6 229 246	6 40 30	-1 637 638	7 204 216	6 430 11	-6 40 25	-8 410 62	0 390 426
-13 135 44	14 430 91	7 232 247	7 9 40	1 289 289	7 42 43	1 H=1	-7 147 145	-7 501 613	1 500 479
-7 612 634	15 430 91	8 399 416	9 44 96	2 35 25	1 490 493	-15 430 81	-4 260 193	-6 525 551	2 283 297
-4 910 8	K=3 H=0	10 1 2	11 447 431	3 90 86	4 224 222	-14 140 132	-3 255 243	-5 625 624	3 59 72
-4 445 455	11 335 324	-16 124 121	-12 37 88	4 37 39	3 379 377	13 237 188	-2 127 149	-6 299 297	4 482 507
-1 171 173	12 221 167	-15 167 158	-15 167 158	-4 137 136	A 42*	-12 42 5	5 192 207	-2 641 635	3 375 360
1 624 684	3 197 186	-14 500 528	14 50 46	6 214 222	7 42 59	-11 186 163	0 394 77	0 341 255	6 122 121
4 374 359	4 105 89	-13 169 177	13 367 371	7 135 142	8 42 33	-10 41 16	1 39 5	1 612 622	7 171 208
4 1162 1144	5 786 729	-12 184 154	K=2 H=3	8 321 327	9 61 59	-9 40 89	2 399 25	2 399 65	8 430 68
7 1074 405	6 432 402	-11 451 408	-11 451 408	10 42 38	10 42 38	10 113 105	3 406 46	3 406 402	K=2 H=2
0 119 133	7 41 22	-10 248 270	-10 248 270	10 42 38	11 203 198	-7 311 354	4 99 86	4 161 147	-10 430 28
11 129 201	8 328 314	-9 199 210	-13 762 722	-11 42 139	K=4 H=5	-6 38 44	5 441 424	5 410 24	-9 162 168
15 139 26	9 60 69	-8 173 181	-12 49 73	K=3 H=4	-7 207 211	-5 52 68	6 441 64	6 251 261	-8 43 3
K=0 H=2	10 185 180	-6 274 12	-10 47 84	-12 43 79	-12 43 79	7 820 179	7 820 179	7 349 352	-7 144 88
-17 711 720	11 205 196	-4 147 133	-9 628 604	-11 230 232	-9 292 294	-3 242 243	8 196 186	8 327 337	-6 153 145
-10 720 721	12 43 21	-3 67 84	-8 338 344	-10 293 280	-4 589 593	-2 35 37	9 43 42	9 185 185	-5 43 26
-8 113 59	13 215 206	-2 143 147	-7 44 9	-9 115 90	-8 149 142	-1 506 479	10 661 657	10 430 17	-4 183 172
-5 121 117	14 240 231	-1 240 231	-1 240 231	0 83 74	-2 239 222	-4 113 105	11 430 74	11 430 74	10 240 212
-4 244 226	0 537 520	0 220 219	-5 171 154	-7 530 520	-1 430 83	1 174 186	K=3 H=8	K=2 H=1	-10 255 575
-7 550 538	1 362 363	2 228 674	-4 207 218	-6 551 562	0 148 126	2 379 393	-10 430 68	-12 179 169	-1 105 169
0 951 1012	2 253 248	3 599 613	-3 207 210	-5 72 72	1 430 16	3 710 737	-11 120 129	0 402 413	0 402 413
4 242 248	3 506 492	4 242 248	-2 325 319	5 501 488	7 330 333	7 330 757	-10 87 45	-10 87 45	2 202 205
4 394 341	4 430 69	5 298 302	-1 117 165	-3 400 3	8 430 35	5 233 238	-7 86 88	-8 255 252	3 375 360
4 338 377	5 400 397	6 622 627	0 39 29	-2 148 155	4 203 209	5 330 66	-6 42 46	-8 255 251	4 430 24
0 698 673	6 43 75	7 404 429	1 267 273	-1 329 351	5 43 14	7 1129 1130	-5 146 149	-7 282 287	5 305 301
10 430 429	7 430 429	8 430 429	9 40 25	0 154 155	6 87 125	9 1000 1000	-4 42 22	-6 84 101	6 162 165
K=0 H=3	8 185 187	9 104 91	3 174 175	4 44 49	K=6 H=10	10 500 511	-2 42 53	-4 469 465	K=3 H=12
-19 415 470	9 152 140	10 180 192	4 42 5	1 2 57	-15 430 50	10 500 511	-1 42 53	-3 253 245	-5 145 96
-11 681 659	K=1 H=1	11 422 422	5 37 53	3 161 161	-14 43 30	11 701 710	0 161 153	-2 212 219	-4 43 71
-9 246 246	-15 43 30	12 83 69	6 38 15	4 191 201	-14 260 266	12 301 304	0 161 153	-2 212 219	-4 43 71
-4 403 400	-14 77 6	13 46 27	7 39 27	5 175 175	-17 260 266	13 129 130	7 820 179	7 820 179	7 186 184
-9 587 609	-13 42 117	15 272 300	8 80 63	6 147 143	-11 41 29	K=2 H=7	2 42 57	0 738 746	-2 430 16
-10 180 174	-12 83 93	K=2 H=2	9 130 142	7 42 38	-17 273 310	-13 430 10	3 363 388	1 106 131	-1 42 77
1 285 281	-11 123 124	-14 398 400	10 308 311	8 42 47	-9 142 143	-12 430 86	4 170 153	2 580 585	0 443 455
3 411 411	-10 39 39	-11 451 450	11 451 450	9 43 43	-10 39 39	-12 430 86	5 182 182	5 182 182	1 162 162
7 369 378	-9 93 76	-12 136 150	12 185 204	10 430 9	-6 175 178	-10 95 61	7 43 45	4 84 95	2 375 374
11 230 280	-8 456 450	-11 48 112	13 43 11	11 115 108	-9 188 183	-9 59 78	8 138 150	5 214 218	3 341 345
19 114 866	-7 124 120	-9 278 294	K=3 H=8	12 268 274	-4 35 40	-8 41 46	9 222 207	6 85 74	K=1 H=13
19 600 834	-4 807 821	-7 15 152	-11 275 302	-9 430 11	-10 171 173	-7 60 62	K=4 H=6	8 7 43	-10 43 12
-14 527 515	-2 751 770	-6 83 86	-10 121 119	-6 430 14	-1 458 479	-4 78 89	-2 43 40	9 430 11	-8 106 104
-17 738 1879	-1 759 795	-5 240 248	-9 176 146	-5 524 544	0 114 113	-3 323 340	-2 43 27	10 430 19	-7 43 76
-10 955 903	0 742 798	-4 162 177	-8 411 424	-4 269 281	1 396 401	-2 128 123	-1 182 184	K=3 H=10	-6 42 11
-8 223 292	1 494 497	-3 40 16	-7 539 574	-3 86 80	2 302 302	-1 607 599	0 430 28	-7 226 257	-5 42 33
-6 1115 1136	2 667 647	-2 92 270	-6 507 500	-2 181 190	3 349 353	0 499 542	-2 184 194	-7 226 257	-6 42 11
-4 750 843	3 708 713	-1 183 193	-5 58 81	-1 430 30	4 184 185	1 87 115	2 287 250	-6 498 497	-3 42 18
-2 662 766	4 594 552	0 129 131	-3 40 59	0 167 175	5 511 516	2 350 345	3 43 10	-5 264 285	-2 42 75
0 213 215	5 161 159	1 206 206	2 39 40	1 235 246	6 554 527	3 275 269	K=1 H=9	-4 162 165	-1 264 281
2 325 370	6 254 255	3 308 331	-1 247 255	-1 247 255	7 108 96	5 1302 1345	-13 162 173	-2 251 259	1 204 205
4 580 587	7 652 670	3 467 479	0 39 0	0 330 307	0 631 639	6 581 605	-12 86 78	-1 86 93	-2 195 192
0 180 180	8 344 327	4 562 566	1 39 48	4 430 280	10 539 544	7 534 513	-11 550 572	0 86 70	3 238 227
16 120 16	9 149 126	5 224 232	2 39 39	6 430 93	11 54 54	8 282 282	-10 249 249	1 183 181	6 430 12
10 212 254	10 405 399	6 307 324	3 40 40	3 40 40	17 229 249	9 245 251	-9 357 350	2 449 434	5 254 261
14 139 2	11 315 304	7 44 31	4 108 113	7 430 51	13 311 314	10 150 157	-8 41 65	3 324 327	6 430 80
14 141 135	13 249 250	8 265 269	5 41 85	-15 102 126	14 430 110	12 290 290	-7 380 377	4 313 319	7 42 108
-13 140 67	14 91 108	9 585 618	6 41 85	-15 102 126	K=2 H=11	13 315 316	-5 640 640	6 430 7	6 410 420
-17 136 104	16 111 101	11 541 514	7 281 240	-14 430 74	-14 430 64	-11 430 24	-4 151 142	-6 430 142	-9 430 83
-17 701 679	K=2 H=1	12 49 28	9 268 260	-12 303 283	-11 430 56	-10 430 21	-3 231 246	7 430 74	-8 430 74
-9 361 373	-15 43 18	14 50 34	10 231 244	-11 268 250	-12 61 100	-9 100 145	-2 323 344	K=1 H=11	-7 43 28
-7 082 045	-13 43 33	11 87 96	-8 536 540	-11 255 147	-11 430 67	-8 430 12	-1 212 183	-12 204 179	-6 87 92
-1 491 568	-12 43 58	-12 50 67	12 44 44	-8 499 463	-10 430 58	-4 42 58	-10 430 58	-10 430 58	-4 43 41
1 202 226	-12 157 167	-11 140 140	K=4 H=3	3 -7 37 50	-9 295 311	-6 42 56	1 421 430	-10 150 177	-4 43 41
3 733 857	-11 169 177	-11 134 155	-8 78 113	-6 318 318	-8 423 420	-5 212 236	2 38 58	-9 527 544	-3 43 42
4 636 682	-10 72 98	-9 49 2	-7 144 153	-5 748 710	-7 224 227	-4 287 291	3 39 75	-8 305 291	-2 192 209
0 604 681	-9 73 99	-8 11 120	9 154 165	-14 3 754	-10 430 75	10 156 156	-10 249 249	-1 183 184	-1 218 213
11 387 356	-8 100 106	-7 441 427	-5 471 474	-3 32 6	-5 38 73	-2 288 294	5 40 70	-4 41 20	-2 211 211
13 138 69	-7 243 248	-6 150 147	-4 257 258	-2 380 394	-4 120 113	3 2	6 41 20	-5 1034 1042	1 217 216
15 141 13	-3 642 601	-3 325 331	-3 43 94	-1 253 255	-6 684 659	0 233 253	8 42 29	-4 100 87	3 430 81
-17 373 419	-3 662 608	-5 114 111	-1 42 111	-1 42 111	-1 625 611	1 166 135	10 236 236	-3 311 316	-3 87 87
-4 532 633	-2 117 119	-2 79 90	0 42 102	2 45 36	-1 613 612	4 39 13	-10 430 95	-8 42 29	5 123 115
0 202 197	-1 53 58	-1 163 175	1 42 40	4 114 121	0 187 157	3 757 756	-11 381 364	-1 925 986	6 415 429
7 400 442	0 235 270	0 45 14	2 42 40	4 114 121	1 91 101	4 330 331	12 304 318	0 380	

Fourier peaks which were not greatly different from the highest background noise peaks.

The X-ray studies showed that at distances less than 2.84 Å from the hydroxyl oxygen atom O(5), there are four oxygen atoms which might participate in hydrogen bonding through the hydrogen atom H(5). These distances are to two atoms O(5) in neighbouring molecules (2.73 Å), to a water oxygen atom (2.84 Å) and to the oxygen atom O(4) of the same molecule. It is difficult to reach reliable conclusions from the well-established heavier atom geometry concerning the orientation of the 5-hydroxyl group in the crystal, since no postulated H(5) position gives a collinear hydrogen bonding arrangement O(5)–H(5)---O'.

The present three-dimensional neutron diffraction study was undertaken primarily in order to provide experimental evidence for the averaged position of the H(5) proton at room temperature.

Experimental

The crystal data were assumed to be those reported by Bolton (1965), *i.e.*

$$\begin{aligned} a &= 12.714 \pm 0.003 \text{ \AA}, & \beta &= 94^\circ 24 \pm 5'. \\ b &= 3.676 \pm 0.003, & Z &= 4 \text{ formula units/cell.} \\ c &= 12.949 \pm 0.004; & \text{Space group: } &P2_1/n. \end{aligned}$$

The crystal used for neutron data collection measured 3.6 mm along **b**, with a somewhat irregular cross section of average area 0.6 mm². This crystal, supplied by

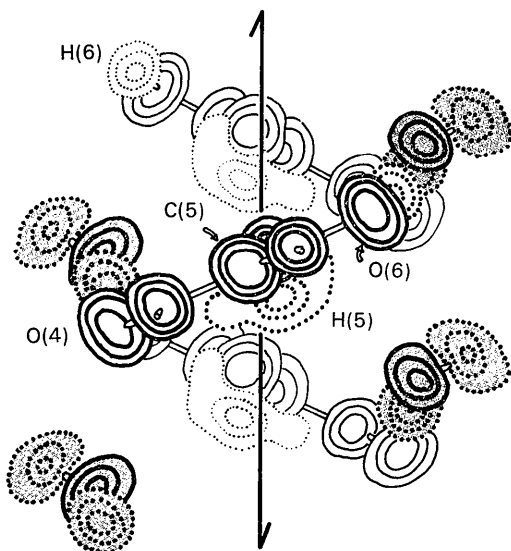


Fig. 2. The three-dimensional Fourier synthesis of the neutron scattering density showing the environment of atom H(5). The positive direction of *x* is toward the viewer, normal to the page. Water molecule peaks are shown shaded. Only the ring atoms C(4), C(5), C(6) and their substituent carbonyl or hydroxyl group atoms are shown for each molecule. The atoms heavily contoured correspond to the shaded molecule in the centre of Fig. 5. The screw axis along *y* which runs through the centre of the Figure is at $x = -\frac{1}{4}$, $z = +\frac{1}{4}$.

Dr Bolton, was the largest in the same batch from which the crystal used for his X-ray data collection was selected.

The diffracted intensity data were obtained using a monochromatic neutron beam ($\lambda = 1.09 \text{ \AA}$) from the HIFAR reactor, of flux $6 \times 10^6 \text{ n.cm}^{-2}\text{sec}^{-1}$ at the specimen. The diffractometer was operated in the $\theta:2\theta$ step-scanning mode, the crystal being mounted with **b** along the φ axis. The intensities were measured for 1174 non-symmetry related reflexions with $\sin \theta/\lambda < 0.6$, of which 303 reflexions were unobservably weak. The latter were assigned intensities one half the minimum observable value. The data were not corrected for the neutron absorption effect arising from the incoherent scattering by the hydrogen atoms.

The refinement of the structure parameters

Initially, the Fourier synthesis of nuclear scattering density (Fig. 1) was calculated with phases for the observed $h0l$ neutron structure amplitudes based on the X-ray results. Coherent neutron scattering lengths were assumed to be H, -0.378 ; C, 0.661 ; N, 0.940 ; O, $0.577 \times 10^{-12} \text{ cm}$ (*International Tables for X-ray Crystallography*, 1962). The crescent of negative scattering density surrounding the atom O(5) in this projection may be attributed in part to diffraction ripple, but there is also a strong indication that H(5) is not in a well-localized position. A three-dimensional structure determination was then undertaken.

A cycle of full-matrix least-squares, in which the atomic positional and thermal parameters reported by Bolton (1965) were varied, was calculated with three-dimensional data. In addition, anisotropic thermal parameters were varied for the hydrogen atoms, with initial values assumed to be the same as those of the heavier atoms to which they are covalently bonded. From the large increase in thermal parameters for atom H(5), it was suspected that this atom might not be in the position suggested by Bolton. Also, a shift of 0.28 \AA in the position of the water oxygen nucleus revealed an error in the listing of Bolton's positional parameters for this atom.* A three-dimensional Fourier synthesis of neutron scattering density was calculated, using calculated structure factor phases based on the revised atomic parameters, but with atom H(5) omitted. In this map (Fig. 2), atom H(5) corresponded to the elongated trough of negative neutron scattering density with a centre corresponding to a dihedral angle of about 70° between the planes of the pyrimidine ring and the hydroxyl group C(5)–O(5)–H(5). This represents a twist of about 80° from the orientation suggested by Bolton.

Full-matrix least-squares refinement was then carried out with standard deviations in observed structure

* Bolton (1965) gives the *y* coordinate for atom O(7) (H₂O) incorrectly in Table 1 as 0.5407 instead of 0.4593 . The reported interatomic distances involving this atom are correct.

amplitudes given by

$$\sigma(F) = \sigma_e + 0.05F,$$

where σ_e = estimated standard deviation derived from experimental counting statistics. Atomic positional and anisotropic thermal parameters were varied for all atoms, including H(5). After four cycles of least squares, convergence was obtained with an R index of 0.092 including all reflexions, or 0.067 excluding the unobserved reflexions. With the unobserved reflexions given zero weight in the least-squares calculations, two cycles of least-squares refinement again gave convergence with an R index of 0.05. The final atomic positional and thermal parameters, with e.s.d.'s derived

from this final refinement, are given in Table 1 and the observed and calculated structure factors are listed in Table 2.

Discussion of the structure

(i) The molecular geometry

Neutron diffraction confirms the molecular structure as 2,4-dioxo-5,6-dihydropyrimidine (*i.e.* 5,6-dihydroxyuracil). A dihedral angle of 67° is observed between the plane of the 5-hydroxyl group C(5)O(5)H(5), and the best least-squares plane through the pyrimidine ring (Table 3). The molecular configuration is shown in Fig. 3, together with ellipsoidal representations of atomic thermal vibration. It is emphasized that the

Table 3. *Least squares planes with atomic displacements*

The planes, referred to the crystallographic axes, are in the form $AX + BY + CZ = D$, with X, Y, Z in Å units. Planes (1) and (2) are best least-squares planes, with all atoms equally weighted. The planes are as follows:

- (1) Plane through the atoms of the pyrimidine ring (present neutron analysis).
- (2) Plane through the atoms of the pyrimidine ring (X-ray analysis; Bolton, 1965).
- (3) Plane through the atoms of the 5-hydroxyl group, *i.e.* C(5), O(5), H(5) (present neutron analysis).
- (4) Plane through the atoms of the 5-hydroxyl group, *i.e.* C(5), O(5), H(5) (X-ray analysis; Bolton, 1965).
- (5) Plane through the atoms of the water molecule.
- (6) The crystallographic plane (010).

(i) Plane coefficients

	<i>A</i>	<i>B</i>	<i>C</i>	<i>D</i>
(1)	0.02067	0.89837	0.43485	2.89513
(2)	0.01443	0.89783	0.43679	2.89718
(3)	-0.32140	-0.02452	0.07267	3.60057
(4)	0.13672	0.95052	0.26483	2.27015
(5)	-0.28145	0.83358	0.49967	3.94497
(6)	0	1.0	0	0

(ii) Dihedral angles

Planes	Angle	Planes	Angle
(1) (3)	+67.3 °*	(1) (6)	26.1 °
(2) (4)	-12	(2) (6)	26.1
(1) (5)	+17.9 *	(3) (6)	91.4
		(5) (6)	33.5

(iii) Displacements of atoms and symmetry elements from the planes

Positive displacements are in the sense outwards from the crystallographic origin towards the plane. The e.s.d.'s in atomic displacements are shown in brackets. Displacements and their e.s.d.'s are in units of Å × 10³.

Atoms forming the planes

	Plane (1) neutron	Plane (2) X-ray
N(1)	-1 (2)	+6 (3)
C(2)	+4 (2)	-5 (3)
N(3)	-7 (2)	-1 (3)
C(4)	+6 (2)	+6 (3)
C(5)	-3 (2)	-6 (3)
C(6)	+1 (2)	0 (3)

Other displacements from plane (1)

O(2)	+8 (3)	H(1)	+63 (6)
O(4)	+6 (3)	H(3)	-31 (6)
O(5)	+51 (3)	H(5)	-714 (10)
O(6)	+24 (4)	H(6)	+136 (6)

Crystallographic centre at (0, 0, ½): -80

Crystallographic centre at (0, 1, 0): +407

* The planes making this angle intersect in a line approximately parallel to **a**. When viewed from the crystallographic origin along the positive direction *x*, a positive angle is a clockwise twist with respect to the plane (1).

dihedral angle of 67° is an average value calculated using the position of the 'thermal' centroid of the H(5)proton.

The pyrimidine ring atoms are very nearly coplanar (Table 3). There are small but highly significant out of plane displacements of all ring substituent atoms, except possibly O(4), which give more nearly collinear intermolecular hydrogen bonds than would otherwise be the case.

The bond lengths in dialuric acid and the water molecule are listed in Table 4 with minimum possible values after correction for anisotropic thermal motion and with corrections assuming the 'riding' mode of thermal motion (Busing & Levy, 1964). The latter assumption provides a reasonable model for the hydrogen atom behaviour and at least an indication of the expected lengthening for the bonds between the heavier atoms. Thus the bond length corrections within the pyrimidine ring appear to be negligibly small, those for the C–O bonds are about 0.01 \AA , those for N–H and O–H bond lengths somewhat greater, and for the O(5) H(5) bond length a very large correction (0.11 \AA) is obtained. The difference between the two O–H bond lengths in the water molecule is insignificant after thermal corrections are applied. The bond lengths and angles without thermal corrections are shown in Fig. 4(a) and (b) for the neutron and X-ray analyses, re-

spectively. The results are the same within experimental error, except possibly for the bond length N(1)–C(6) for which the difference (0.014 \AA) has an e.s.d. of 0.005 \AA .

Table 4. *Thermal corrections to the bond lengths*

Column (1): uncorrected values; (2): the minimum values with corrections assuming the anisotropic thermal parameters given in Table 1; (3): the corrected values assuming the 'riding' mode of thermal motion.

Bond	(1)	(2)	(3)
N(1)–C(2)	1.349 Å	1.349 Å	1.352 Å
C(2)–N(3)	1.349	1.349	1.350
N(3)–C(4)	1.372	1.372	1.375
C(4)–C(5)	1.416	1.416	1.416
C(5)–C(6)	1.357	1.357	1.357
C(6)–N(1)	1.366	1.366	1.370
C(2)–O(2)	1.219	1.220	1.228
C(4)–O(4)	1.238	1.239	1.250
C(5)–O(5)	1.349	1.350	1.360
C(6)–O(6)	1.297	1.299	1.311
N(1)–H(1)	1.019	1.021	1.038
N(3)–H(3)	1.035	1.036	1.050
O(5)–H(5)	0.923	0.965	1.035
O(6)–H(6)	1.007	1.008	1.019
O(W)–H(1,W)	0.930	0.930	0.941
O(W)–H(2,W)	0.947	0.947	0.949

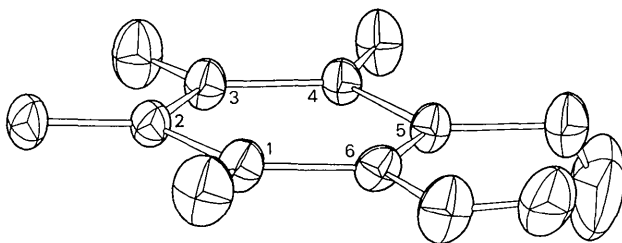


Fig. 3. The molecular configuration with ellipsoidal representations of the anisotropic thermal parameters. These are 50% probability ellipsoids.

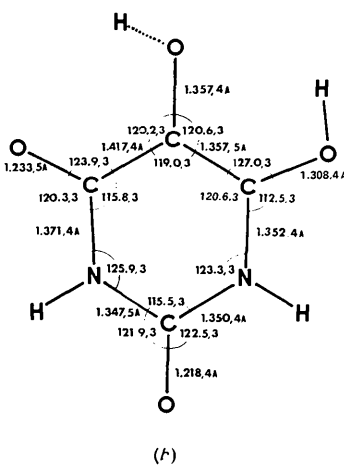
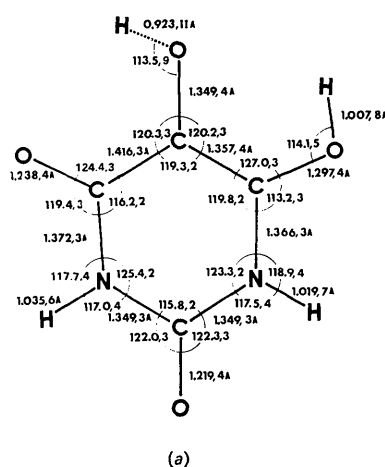


Fig. 4. The bond lengths and angles (uncorrected for the effects of anisotropic thermal motion). (a) The present neutron analysis, (b) the X-ray analysis, Bolton (1965).

(ii) *The molecular packing and hydrogen bonding*

The molecular packing and hydrogen bonding in dialuric acid monohydrate are shown in Figs. 2 and 5. The b projection of the crystal structure was shown by Bolton (1965, Fig. 2). The hydrogen bonding distances and angles and other close intermolecular distances are listed in Table 5.

(iii) *The environment of the 5-hydroxyl group*

From qualitative considerations, the planar conformation I is expected for the isolated dialuric acid molecule. This would maximize the attractive interac-

tions between the protons H(5) and H(6) and the lone pair electrons on oxygen atoms O(4), O(5) and O(6), and permit the most effective participation of atoms O(5) and O(6) in the delocalized π -bonding of the oxypyrimidine system.

In the crystal structure, the O(6)H(6) hydroxyl group forms a strong hydrogen bond with a water molecule [O(6)---O(W) distance 2.57 Å; H(6)---O(W) distance 1.57 Å] with atoms O(6) and H(6) only slightly displaced from the pyrimidine ring plane (Table 3, iii). For this hydroxyl group, the predicted conformation for an isolated molecule and that which is observed in the crystalline hydrate are closely similar.

For the O(5)H(5) hydroxyl group, however, the postulated planar conformation would result in a close intermolecular approach (2.0 Å) between atoms H(5) and the water hydrogen atom H(1, W) which is hydrogen bonded to the carbonyl oxygen atom O(4). This would be a repulsive interaction, since the H---H distance is considerably less than the van der Waals distance (2.4 Å; Pauling, 1960). Other intermolecular interactions involving H(5) in this postulated position would be with two oxygen atoms O(5), at distances 1.4 and 2.2 Å along the positive and negative y directions. These interactions might be described as forming a weak bifurcated hydrogen bond. The hydrogen

Table 5. Intermolecular distances and angles with *e.s.d.*'s

The *e.s.d.*'s are shown in brackets as 1000 $\sigma(d)$ Å and $10\sigma(\theta)$ °. Atoms not in the crystal chemical unit (*i.e.* not listed in Table 1) are specified by a subscript. The four-digit subscript denotes how the atomic parameters can be derived from the corresponding atom in the crystal chemical unit. The first three digits code a lattice translation, *e.g.* 564 means a translation of $(5-5)a + (6-5)b + (4-5)c$ or $(b-c)$. The fourth digit specifies one of following operations:

1:	x, y, z	3:	$\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$
2:	$-x, -y, -z$	4:	$\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z$

(i) Hydrogen bonds, excluding interactions involving O(5) H(5)

Distance	$d, \sigma(d)$	Angle	$\theta, \sigma(\theta)$
N(1)---O(2) ₅₅₅₃	2.764 (4) Å	N(1)---H(1)···O(2) ₅₅₅₃	173.4 (6)°
H(1)---O(2) ₅₅₅₃	1.749 (7)	H(1)···O(2) ₅₅₅₃ ---C(2) ₅₅₅₃	130.5 (3)
N(3)---O(4) ₅₅₆₂	2.792 (4)	N(3)---H(3)···O(4) ₅₅₆₂	176.8 (5)
H(3)---O(4) ₅₅₆₂	1.758 (6)	H(3)···O(4) ₅₅₆₂ ---C(4) ₅₅₆₂	124.1 (3)
O(6)---O(W) ₄₅₅₃	2.571 (7)	O(6)---H(6)···O(W) ₄₅₅₃	169.8 (7)
H(6)---O(W) ₄₅₅₃	1.574 (9)	H(6)···O(W) ₄₅₅₃ ---H(1, W) ₄₅₅₃	118.9 (8)
		H(6)···O(W) ₄₅₅₃ ---H(2, W) ₄₅₅₃	125.3 (8)
		H(6)···O(W) ₄₅₅₃ ···H(5) ₄₆₅₃	98.7 (5)
O(W)---O(2) ₅₆₆₂	2.830 (7)	O(W)---H(2, W)···O(2) ₅₆₆₂	162.3 (9)
H(2, W)---O(2) ₅₆₆₂	1.913 (10)	H(2, W)···O(2) ₅₆₆₂ ---C(2) ₅₆₆₂	124.7 (4)
O(W)---O(4)	2.834 (7)	O(W)---H(1, W)···O(4)	169.8 (9)
H(1, W)---O(4)	1.914 (7)	H(1, W)···O(4)---C(4)	127.9 (4)
		O(2) ₅₆₆₂ ···O(W)···O(4)	87.9 (2)

(ii) Interactions involving the 5-hydroxyl group*

Distance	$d, \sigma(d)$	Angle	$\theta, \sigma(\theta)$
O(5)---O(5) ₄₅₅₃	2.744 (5) Å	C(5)---O(5)···O(5) ₄₅₅₃	140.2 (3)°
O(5)---O(5) ₄₄₅₃	2.744 (5)	C(5)---O(5)···O(5) ₄₄₅₃	118.6 (3)
O(5)---O(W) ₄₄₅₃	3.068 (7)		
O(5)---O(W) ₄₅₅₃	2.825 (7)	C(5)---O(5)···O(W) ₄₅₅₃	110.7 (3)
H(5)---O(5) ₄₅₅₃	3.043 (11)		
H(5)---H(5) ₄₅₅₃	2.23	H(5) ₄₅₅₃ ···H(5)···H(5) ₄₄₅₃	111
H(5)---O(5) ₄₄₅₃	1.945 (13)	O(5)---H(5)···O(5) ₄₄₅₃	143.7 (11)
		H(5)···O(5) ₄₄₅₃ ---C(5) ₄₄₅₃	136.7 (5)
		O(5)---H(5)···O(W) ₄₄₅₃	117.2 (10)
H(5)---O(W) ₄₄₅₃	2.534 (16)	H(5)···O(W) ₄₄₅₃ ---H(1, W) ₄₄₅₃	80.6 (7)
		H(5)···O(W) ₄₄₅₃ ---H(2, W) ₄₄₅₃	118.0 (8)
H(5)---O(W) ₄₅₅₃	3.236 (16)		

(iii) Close non-bonded intermolecular interatomic distances†

Distance	d	Distance	d
C(2)---N(1) ₅₄₅₁	3.326 Å	H(1)---C(2) ₅₅₅₃	2.705 Å
N(3)---C(6) ₅₄₅₁	3.475	H(3)---C(4) ₅₅₆₂	2.657
C(4)---C(5) ₅₄₅₁	3.321	H(6)---H(1, W) ₄₅₅₃	2.181
C(4)---C(6) ₅₄₅₁	3.491	H(6)---H(2, W) ₄₅₅₃	2.258
C(6)---O(6) ₅₄₅₁	3.295		
O(6)---O(6) ₅₆₅₂	3.335	O(W)---O(5) ₄₄₅₃	2.825
		O(W)---O(5) ₄₅₅₃	3.068
		O(W)---O(5)	3.424

* Distances and angles are with respect to the position of the thermal centroid of atom H(5).

† This list includes all distances which are within 0.2 Å of the sum of the appropriate van der Waals radii (C, 1.7; N, 1.5; O, 1.4; H, 1.2 Å; Pauling, 1960).

bonded chains with H(5) atoms in such positions are not observed.

A twist of the O(5)–H(5) bond in the opposite sense, *i.e.* away from the line of centres O(5)---O(5'), would weaken the hydrogen bond O(5)–H(5)---O(5'), but would strengthen the attractive interaction O(5)–H(5)---O(W) with the water oxygen atom at the bottom right of Fig. 2, by decreasing the H(5)---O(W) distance from 2.5 Å and increasing the angle at H(5) from 117°. The water molecule would then become involved in four, rather than three, hydrogen bonds, and these would be tetrahedrally disposed.

It appears that, within the observed range of twist of the O(5)–H(5) bond about the C(5)–O(5) bond, no one position is particularly favourable for intermolecular hydrogen bonding.

The greater part of this work was carried out while B.M.C. was a Senior Rothmans Research Fellow at Sydney University. Research facilities were kindly made available by Dr H.C. Freeman of the School of Chemistry, and by a grant from the Australian In-

stitute for Nuclear Science and Engineering. The work was completed with support by a research grant NB-02763 from the U.S. Public Health Service, National Institutes of Health. Computer programs for IBM 7040 used in this work were written by Mrs Suzanne Hogg and Dr G.W. Cox (A.A.E.C. Research Establishment). Programs used for the IBM 7090 were written by Dr R. Shiono (University of Pittsburgh) and Dr C.K. Johnson (Oak Ridge National Laboratory, Tennessee). We thank the A.A.E.C. Reactor Operations Section for assistance with data collection.

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The Crystal Structures of Two Polymorphs of 5,5'-Diethylbarbituric Acid (Barbital)

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(Received 21 May 1968 and in revised form 13 November 1968)

Crystal morphological, X-ray and infrared spectral data are presented for the identification of three (I, II and IV) of the four reported polymorphs of 5,5'-diethylbarbituric acid (barbital). Three-dimensional X-ray crystal structure determinations of barbital I and II are reported. The crystal data are: I (trigonal, m.p. 190°C) $a=26.921$, $c=6.828$ Å (hexagonal lattice), space group $R\bar{3}$, with 18 molecules per cell; II (monoclinic, m.p. 183°C) $a=7.120$, $b=14.162$, $c=9.810$ Å, $\beta=89^\circ 14'$, space group $C2/c$ with 4 molecules per cell. For barbital I X-ray intensity data were collected from two different crystals and two independent structure determinations (Ia, Ib) were carried out. These agreed within experimental error. The X-ray intensity data (1526, 1617 and 840 reflections in Ia, Ib and II) were collected with a four-circle automatic diffractometer. Refinement of atomic positional and anisotropic thermal parameters was by full-matrix least-squares, resulting in final R values of 0.057, 0.041 and 0.062 for Ia, Ib, II, excluding the unobservably weak reflections. All hydrogen atoms were found. The molecule is in the 2,4,6-trioxo tautomeric form in both I and II. The molecular point symmetry is approximately 2 *mm*, but with distortions in the barbiturate ring and hydrocarbon chain which are most marked in I. Molecules are linked by NH...OC hydrogen bonds to form ribbons in which the barbiturate rings are almost coplanar, although the mode of hydrogen bonding is different in I and II. Van der Waals interactions are of greater importance in the stable form I. Variations of 0.014 Å in C–N ring bond lengths are near the limit of experimental error, but appear to be systematic and may be related to hydrogen bonding effects. The atomic thermal vibrational behaviour is strikingly similar in I and II.

Introduction

Since 1903 when Fischer and von Mering discovered the hypnotic action of 5,5'-diethylbarbituric acid (also

known as barbital, veronal, or diemal, Fig. 1†), the relationship between chemical structure and drug action

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† The atomic nomenclature in the present work was chosen to conform as closely as possible to the chemical nomenclature. A twofold rotation axis of crystallographic symmetry passes through atoms O(2), C(2) and C(5) in the case of barbital II.