

Fig. 4. A stereoscopic view of the molecular packing in the unit cell of dimethylammonium copper(II) formate.

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The Crystal and Molecular Structures of Reaction Products from γ-Irradiation of Thymine and Cytosine: *cis*-Thymine Glycol, C₅H₈N₂O₄, and *trans*-1-Carbamoyl -imidazolidone-4,5-diol, C₄H₇N₃O₄

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As part of a study on the mutagenetic effects of ionizing radiation on nucleic acids, solutions of thymine and cytosine were subjected to γ -radiation. In both cases the reaction conditions were the same; however, the products differed significantly. The product of the thymine reaction was *cis*-thymine glycol (I), $C_sH_8N_2O_4$ [space group $P2_12_12_1$ with a=9.745 (6), b=10.806 (6), c=6.282 (4) Å]. The reaction on the cytosine molecule involved a rearrangement of the six-membered ring to give an imidazolidone derivative (II), $C_4H_7N_3O_4$ [space group *Pbca* with a=13.228 (8), b=13.260 (8), c=7.139 (4) Å]. The calculated crystal densities are 1.61 g cm⁻³ for (I) and 1.71 g cm⁻³ for (II). Both structures were solved by the symbolic addition procedure. Intensities were collected on an automatic diffractometer (Cu K α radiation) and refined to final R values of 0.052 for (I) and 0.064 for (II). Hydrogen bonding plays a significant role in the packing systems of both molecules.



Introduction

The radiation chemistry of the nucleic acid bases, thymine, cytosine and uracil, has been the subject of extensive research in attempts to determine the molecular origin of biological radiation damage (Fahr, 1969). When solutions of thymine and cytosine were subjected to y-radiation, under the same reaction conditions, the products were expected to be *cis* and *trans* glycols of the reactant molecules (Ekert & Monier, 1960; Ekert, 1962; Khattak & Green, 1966). Isolation of the products of the thymine reaction was recently accomplished by Hahn & Wang (1972) who identified the products as *cis* and *trans* thymine glycols and characterized the stereochemistry of both isomers by chemical means. The structure of the *cis*-thymine glycol (I) was confirmed by X-ray analysis (this work). When the products from the cytosine reaction were isolated and purified by Hahn & Wang. it was found that the spectral evidence was not conclusive and an X-ray analysis was necessary for an unequivocal structure determination (Hahn, Wang, Flippen & Karle, 1973). The X-ray analysis was carried out on the *trans*

isomer and showed it to be an imidazolidone derivative (II) This is the first time a photoreaction on a pyrimidine base has involved a rearrangement of the sixmembered heterocyclic ring. These newly identified imidazolidones are analogs of synthetic nucleosides which have been shown to have broad spectrum antiviral activity (Sidwell, Huffman, Khare, Allen, Witkowski & Robins, 1972). The nucleosides of the imidazolidones, possibly produced in biological systems, may also possess antiviral activity (Hahn *et al.*, 1973).

Experimental

Crystals of both materials were kindly provided by Professor S. Y. Wang of the Johns Hopkins University.

	Table 1. Crystal data	
Molecular formula Crystal size	Molecule I $C_5H_8N_2O_4$ ~(0.90 × 0.40 × 0.15mm)	Molecule II $C_4H_7N_3O_4$ ~(0.25 × 0.25 × 0.12mm)
Space group	$P2_{1}2_{1}2_{1}$	Pbca
a	9·745 (6) A	13·228 (8) A
b	10.806 (6)	13.260 (8)
с	6.282 (4)	7.139 (4)
Molecules per unit cell	4	8
Density (calc.)	1.61 g cm^{-3}	1.71 g cm^{-3}
Source of data	Picker FACS-I diff	fractometer
Radiation	Cu <i>K</i> α(1·5418	Å)
	Ni filter	
Data collection technique	θ -2 θ scan	
Scan width	$2\cdot 2^{\circ} + 2\theta(\alpha_1) - 2\theta(\alpha_2)$	$1.5^{\circ} + 2\theta(\alpha_1) - 2\theta(\alpha_2)$
Scanning speed	2 deg/min	1 deg/min
Background counting time	10 sec	
Maximum sin θ/λ	0.521	
Number of independent reflections	659	1024

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Table 2. Fractional coordinates and thermal parameters with standard deviations

cis-Thymine glycol

The thermal parameters are of the form $T = \exp[-\frac{1}{4}(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^* + 2B_{13}hla^*c^* + 2B_{23}klb^*c^*)]$.

Standard deviations are based solely on least-squares parameters.

	x	у	z	B ₁₁	B_{22}	B ₃₃	B ₁₂	B ₁₃	B_{23}
N(1)	0.3064 (4)	0.1263 (3)	0.0384 (6)	3.0 (1)	2.2 (1)	2.5 (1)	-1·0 (1)	− 0·0 (1)	0.2 (1)
C(2)	0.3080 (4)	0·1774 (4)	-0·1547 (6)	1.8 (1)	$2 \cdot 4(1)$	1.9 (1)	0.0 (1)	0.3 (1)	-0·4 (1)
Ō(2)	0.2507 (3)	0·1326 (3)	-0.3162(5)	2. 7 (1)	3.0 (1)	1.9 (1)	-0.3(1)	-0·1 (1)	-0·6 (1)
N(3)	0·3788 (3)	0.2879 (3)	-0.1737(6)	2.6(1)	$2 \cdot 3(1)$	1.6 (1)	-0.2(1)	-0.3(1)	0.2 (1)
C(4)	0·4266 (4)	0.3577 (4)	-0.0061 (6)	$2 \cdot 1$ (1)	1.9 (1)	2.0 (1)	0.3 (1)	-0.2(1)	0.2 (1)
O(4)	0·4958 (3)	0·4498 (3)	-0.0322(5)	3.0 (1)	2·3 (1)	2.7 (1)	− 0·8 (1)	-0 •5 (1)	0.4 (1)
C(5)	0·3772 (4́)	0.3139 (4)	0.2134 (6)	2.1 (2)	2.6 (1)	1.4 (1)	-0·3 (1)	<i>−</i> 0·0 (1)	-0.4(1)
O(5)	0.4624 (3)	0.3657 (3)	0.3761 (4)	2.3 (1)	2·9 (1)	2.2 (1)	-0·0 (1)	<i>−</i> 0·3 (1)	-0.7(1)
C(6)	0.3853 (4)	0.1737 (4)	0.2142 (7)	2.4 (2)	2.7 (2)	1.9 (2)	-0.2(1)	0.2 (1)	0.2 (1)
O(6)	0.5264(3)	0.1438(3)	0.1950 (5)	2.6 (1)	2.2 (1)	3.5 (1)	0.3 (1)	-0.2(1)	0.5 (1)
C(7)	0·2325 (5)	0.3618 (5)	0.2544 (8)	2.4 (2)	4.2 (2)	3.2 (2)	0.3 (2)	0.3 (2)	-0.9(2)

Table 2 (cont.)

	x	у	Z
H(1)	0.283 (6)	0.054 (5)	0.065 (10)
H(3)	0.374 (6)	0.316(5)	0.708 (10)
H(O5)	0.540 (7)	0.345(5)	0.305 (10)
H(C6)	0.335 (6)	0.142(6)	0.343 (10)
H(O6)	0.527 (6)	0.072 (6)	0.250(11)
H(7A)	0.213 (6)	0.448 (6)	0.229(11)
H(7 <i>B</i>)	0.167 (7)	0.340 (7)	0.127(12)
H(7C)	0.185 (7)	0.328(6)	0.389 (12)

Table 3. Fractional coordinates and thermal parameters with standard deviations

trans-1-Carbamyl-imidazolidone-4,5-diol

The thermal parameters are of the form $T = \exp \left[-\frac{1}{4} (B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{13}hla^*c^* + 2B_{13}hka^*b^* + 2B_{23}klb^*c^*) \right]$.

Standard deviations are based solely on least-squares parameters.

	x	У	Z	B_{11}	B22	B ₃₃	B_{12}	B_{13}	B_{23}
N(1)	0.4812(2)	0.1487 (2)	0.1299 (3)	1.4 (1)	1.5(1)	2.5(1)	-0.0(1)	0.0(1)	0.3(1)
C(2)	0.5177(2)	0.0559(2)	0.1930 (4)	2.4(1)	2·0 (1)	2·0 (1)	-0.0(1)	-0.2(1)	-0.3(1)
O(2)	0.6064(1)	0.0285(1)	0.1837(3)	1·6 (1)	2.4(1)	3·5 (1)	0·5 (1)	-0.0(1)	0.2(1)
N(3)	0.4396(2)	0.0033(2)	0·2606 (4)	1.9 (1)	1.8 (1)	$3 \cdot 2(1)$	-0.0(1)	0.2(1)	0.6(1)
C(4)	0.3465(2)	0.0606(2)	0.2676(4)	1.8 (1)	2.5(1)	2·7 (1)	0.2(1)	0.1(1)	0.0(1)
O(4)	0.3175(2)	0.0855(2)	0.4517(3)	2·0 (1)	3.7 (1)	2·7 (1)	-0·0 (1)	0.2(1)	0.2(1)
C(5)	0.3708(2)	0.1535(2)	0.1474 (4)	1.6 (1)	2.0(1)	2.8(1)	0.1(1)	-0.1(1)	0.0(1)
O(5)	0.3233(1)	0.1517(2)	-0.0298(3)	2·1 (1)	$2 \cdot 4(1)$	2.8(1)	0.4(1)	-0.6(1)	0.2(1)
C(6)	0.5378(2)	0.2339(2)	0.0852(4)	$2 \cdot 2 (1)$	1.7 (1)	$2 \cdot 2 (1)$	-0.3(1)	-0.3(1)	-0.1(1)
N(6)	0.6365(2)	0.2199(2)	0.0584(4)	1.7 (1)	2.3(1)	5.0(2)	-0.3(1)	0.4(1)	0.7(1)
O(6)	0.4961 (1)	0·3164 (1)	0.0709 (3)	2.4 (1)	1.5 (1)	3.6(1)	0.0 (1)	-0.2(1)	0.2(1)

Table 3 (cont.)

	x	У	Z
H(N3)	0.447 (2)	-0.058(2)	0.315(5)
H(C4)	0.289(2)	0.022(2)	0.214(4)
H(O4)	0.360 (3)	0.114(3)	0.501 (6)
H(C5)	0.353 (2)	0.221(2)	0.211(5)
H(O5)	0.342 (2)	0.093(2)	-0.086(5)
H(N6A)	0.673 (2)	0.277(3)	0.040(5)
H(N6 <i>B</i>)	0.664 (3)	0.160 (3)	0.080 (5)

Information on data collection and physical quanties for both molecules is given in Table 1. Lorentz and polarization corrections were applied and normalized structure factor magnitudes |E|, as well as structure factor magnitudes $|\bar{F}|$, were derived.

The structure of *cis*-thymine glycol (I) was solved by the symbolic addition procedure for noncentrosymmetric crystals (Karle & Karle, 1966), The modified B_{3.}0 formula (Karle, 1970) was used to help confirm the assumption (made in the symbolic addition procedure) that the cosine invariants employed in the initial part of the phase determination are close to unity. The basic set of phases was then expanded by the tangent formula. The resulting molecule was properly oriented but misplaced with respect to a true origin for space group $P2_12_12_1$ and a translation function (Karle, 1972) was calculated which indicated a one-dimensional shift of ± 1.150 Å in the z direction. The correct shift was -1.150 Å. The structure of the imidazolidone (II) was solved by routine application of the symbolic addition procedure for centrosymmetric crystals (Karle & Karle, 1966). Computer

programs written by R. D. Gilardi & S. A. Brenner of this laboratory were used to facilitate use of the above procedures.

The structures were refined by full-matrix leastsquares methods on F values. Program ORFLS (Busing, Martin & Levy, 1962) was used for (1) and program ORXFLS3 (Busing et al., 1971) was used for (II). The function minimized was $\sum w(|F_o| - |F_c|)^2$, where the weighting function w was calculated according to

$$w^{-1} = \sigma_{F^{\parallel}}^{2} = \begin{cases} Q \cdot [P - t_{f}(B_{1} + B_{2})] \\ 4 \cdot Lp \end{cases} \\ \frac{P + C^{2}P^{2} + t_{f}^{2}(B_{1} + B_{2} + C^{2}B_{1}^{2} + C^{2}B_{2}^{2})}{[P - t_{f}(B_{1} + B_{2})]^{2}} + \frac{\sigma_{e}^{2}}{Q} \end{cases}$$

where

Q = attenuator factor,

P = peak count,

- B_1B_2 = background counts.
 - t_f = time factor to put background and peaks on same scale.
 - C = instrumental reliability factor (0.02).



Fig. 1. Stereogram of a molecule of *cis*-thymine glycol (I)

Table 4. Observed and calculated structure factors for
cis-thymine glycol (I)

The columns are the index h, $10|F_o|$, and $10|F_c|$.

н о о	15 222 -226	- 1111-5		0 05 05	15 500 501		· 101 103
21294 1267	13 34 44	5 88 -58	V 249 -244	¥ 267 255	14 49 50	0 203 -218	5 56 +50
4 340 -377	14 00 -02	4 48 47	10 140 -134	10 0 12		113 -109	4 19 -11
						1 100 -000	
01332 1314	15 56 50	1 74 441	11 103 -103	11 21 47	0 04/ 4/18	2	/ 11 20
8 271 256	H 1 2	8 50 -51	12 0 -22	12 237 229	1 513 554	1 12 74	8 178 186
						10 -10	0 348 - 348
10 /1 80	11350 1354		14 14 0	11 42 14	e 111 +126	• 10 •25	
12 47 58	2 51 +50	1 52 -01	H 2 5	14 60 -68	3 82 -92	5 26 69	10 227 224
14 17 -48	3 67. 646	2 97 Hi	0 118 229		4 43 -14	4 31 -36	11 211 +208
1- 10							
M 0 2	• 321 • 324	3 <u>2</u> 4 -30	1 9 42	1 33 -34	2 537 +530	1 1 1 0101	15 50 010
0 212 214	5 189 180	H 2 0	2 269 273	2 40 35	6 245 .247	8 75 73	н 55
1 103 104		A 184 189	1 1 1 1 1 2 1	2 414 -442	1 245 245		1 71 -61
1 146 144	0 779 710	1 104 100	9 190 189	2 414 4405	1 203 203		
2 656 -565	7 571 553	2 155 -155	4 120 130	4 280 .274	8 39 -52	н 47	2 106 -103
3 300 300	0 0 1	4 379 - 340		4 78 -03	0 202 - 210	A 174 -100	3 46 54
3 300 304		1 144 147	7 34 34			0 1.0 -1.00	1 10 10
4 190 179	9 3 3 1 3 2 4	0 034 -011	6 7V V7	0 121 4145	10 158 -153	1 0 -10	4 534 544
9 228 .224	10 255 +261	8 411 -401	7 45 +36	7 162 -154	11 58 55	2 39 +55	5 0 5
		1 1			12 100 -104		4 46 11
C 200 100	11 109 -100	10 110 103	0 200 212		15 104 -100	3 49 37	0 0 01
7 194 194	12 240 245	12 93 100	9 126 123	9 51 -35	13 211 203	4 66 -79	7 84 -78
8 187	11 42 -4	14 91 -98	10 96 98	10 17 18	14 28 26	4 9 26	8 118 -125
4 120 -105	14 44 01	- e i	11 10 10	11 100 1/2	· · ·		4 10, 410,
10 138 144	F 1 3	01249-1307	12 28 4	12 140 127	0 784 +786	7 35 -19	10 22 -29
11 73	1 424 418	1 11 14		13 77 -76	1 222 234	H B 0	11 105 -98
11 14 -13	1 050 010						
12 44 94	2 209 +204	c Zey +242	v 115 131		z /o 78	5 023 +440	
13 73 70	3 100 104	3 17 -3	1 56 54	1 828 +643	3 680 655	4 403 -418	1 237 241
14 128 4122	A 110 -113	A 273 209	2 178 183	2 161 165	4 85 88	4 80 800	2 176 +187
+0155							
н о 4	5 41 +30	5 0 8	3 16 67	59 čr L	5 189 177	P 203 -285	3 0 35
0 202 194	6 28 -15	6 279 -264	4 101 91	4 273 a245	6 63 -74	10 455 #467	4 87 101
1 43/ 440	1 700 190	1 03 401	3 6' 60	3 230 0241	/ 8/ 4/2	15 121 #105	5
2 450 -429	6 131 -131	8 253 +241	6 30 36	6 87 -77	8 368 365	14 31 -28	6 94 97
3 317 - 333	0 360 345	4 48 41	7 47 14	7 145 -145	8 273 375		7 123 126
3 611 4666	• 133 343						
4 280 -273	10 130 141	10 41 31	a 12a 1ol		10 102 #105	1 134 -145	8 0 -2
5 176 -170	11 110 103	11 0 0	9 49 -12	9 365	11 249 251	2 178 -191	9 106 101
0 44 37	15 202 302	15 10 03	10 45 44	10 130 6135	15 144 4144	3 101 143	
7 369 361	13 109 -111	13 32 -44	H 2 7	11 66 -71	13 71 -19	4 235 242	1 7 -24
8 420 -422	14 41 24	ia 30 il	1 100 -101	12 71 -49	14 88 101	6 196 182	2 118 -122
0 -20 -22	14 43 27	12 12 11	104 4103		14 80 101		
9 40 -13	F 1 4	12 42 412	2 Q .B	13 150 132	н 4 3	6 205 257	3 104 -114
10 124 -131	1 209 211	н 22	3 86 -85	H 3 5	0 119 128	7 69 68	+ 0 5
		A1438-1484		1 00 -04			
11 112 -114	5 84 40	01030-1000	- 0 1-	1 44 440	1 00 -43		5 64 465
12 156 151	3 406 390	1 180 184	5 30 45	2 516 510	2 62 63	9 193 195	6 31 3
11 00 .01	A 210 -215	2 708 -700	A 51 53	1 64 199	3 480 441	10 84 -98	н 6 6
12							
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0 150 -158	6 109 115	a 126 133	н 28	5 120 125	4 75 +58	12 150 -156	2 451 568
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2 134 -141	8 43 30	6 46 -100	1 27	7 30 -31	7 229 233	14 73 -77	6 82 .77
1 101 104	0 A3 0A	7 132 -129	2 0 15	A 192 144	8 151 156		A 188 189
e ies -1ez	10 224 -22	0 160 0150	1 20 14	• 121 •131	4 352 +359	1 10 33	10 104 741
5 157 -165	11 146 -145	9 90 -82	н з о	10 78 77	10 252 -255	2 268 -263	75 40 84
A 101 -04	12 4 15	10 83 101	21165 1191	11 52 37	11 198 -201	2 150 -139	14 73 78
/ 225 231	13 83 84	11 195 191	+ 85A +815		15 193 -124	4 300 334	- o t
6 99 104	H 1 5	12 9 6	6 143 138	1 94 -92	13 26 16	5 222 -217	0 546 +558
9 01 08	1 141 4140	13 148 152	8 617 517	2 181 -194		4 10 .49	1 463 467
10 103 194	< ev8 208	1	10 124 -175	3 6 4 2 3 3	0 142 144	1 540 0140	e 10 17
н с в	3 37 -29	н 23	12 95 -101	4 0 -44	1 250 -262	A 258 +258	3 355 362
0 107 -114	A 1A 9	0 85 83	14 78 43	5 108 -98	2 295 308	0 107 .09	A 333 339
. 0 14	14	·	1			10 100 100	2 100 -115
2 0 =34	6 70 83	2 125 125	1 244 258	/ 54 +54	4 60 56	11 49 -29	6 6 19
1 123 -120	7 18	3 91 86	2 110 -115	8 134 -131	5 136 240	12 162 155	7 124 127
- 1 0	0 0 -32		3 100 -775	4 114 110	n ol -81	13 103 041	0 30 433
2 427 437	9 183 -181	5 0 +6	4 75 -72	10 53 +40	7 23 0	14 0 +12	9 231 230
. 738	10 155 -151	6 1 29 1 26	6 76 64				10 78 34
	10 103 -151	1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1			- 131 12*		
6 203 193	11 135 -135	/ -1 -33	U 404 386	1 142 153	A 189 190	1 40 21	11 130 138
8 168 158	12 42 -32	8 103 99	7 88 65	2 55 -64	10 46 +52	2 389 -373	12 0 5
10 221 -221		0 155 141	8 .27 .11	1 80 89	11 10	114 114	آم أم أأ
15 149 514	1 93 485	10 0 24	¥ 350 -342	e 1e3 =198	12 44 -46	4 /7 #85	n 6 2
14 107 99	2 120 124	11 79 83	10 761 -363	5 107 112	H 4 5	5 154 -166	0 199 -203
	1 1 1 1 1 1 1	12 176 170	11 111 -152		0 420 4410	4 260 -251	1 261 -265
1 365 -380	4 23 24	13 113 444	14 322 -328	/ 120 132	1 204 210	7 1 7	5 23 -20
2 355 373	5 114 +125	14 65 71	13 98 -104	н 3 8	2 52 26	8 163 -161	3 176 -172
1 51			14 81	1 44 4	1 147 1.4	0 187 145	A 177 183
			** ** */0	50	143	103	102
• 121 •112	/ 21 -+	0 474 501	H 3 2	2 0 6	4 79 -64	10 0 26	5 50 +44
5 278 272	8 93 83	1 353 +357	1 172 -180	н 🔥 О	5 63 -47	11 12 27	6 357 357
6 346 211	9 9 96	2 285 295	2 403 411	0 179 177	A 154	1 0 99	7 278 - 274
						12	
/ 133 -148	th e1 66	3 367 -560	1 304 3/3	2 007 033	7 104 97	13 20 5	0 144 199
8 306 308	H 1 7	4 82 89	+ 137 -131	4 265 +251	8 22 34	H 5 4	9 304 -309
9 127 -122	1 98 -106	5 0 20	5 144 - 744	6 796 -767	0 87 77	1 76	10 57 73
						1	
10 1/0 +187	2 100 -104	0 00 56	9 104 197	9 ef 38	10 60 -44	2 504 201	11 100 -190
11 97 94	1 52 69	7 49 45	/ 50 -17	10 201 -206	11 54 44	1 261 -265	12 193 187

A detailed derivation of the weighting function is given by Gilardi (1973).

The atomic scattering factors used were those listed in *International Tables for X-ray Crystallography* (1962). All the hydrogen atoms for both molecules were located from difference maps. Their positional parameters were refined and their assigned thermal parameters (set equal to those of the atoms to which they



Fig. 2. Bond distance and angles for (I).

were bonded) were included in the refinement as constants. All data were included in the refinement, no reflections being considered unobserved. The final Rvalues where $R = \sum ||F_o| - |F_c|| / \sum |F_o|$, were 0.052 for (I) and 0.064 for (II). The weighted R values where $R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w F_o^{2}]^{1/2}$, were 0.069 for (I) and 0.045 for (II). Fractional coordinates for all the atoms and thermal parameters for the C, N and O atoms are listed in Table 2 for (I) and in Table 3 for (II). The observed and calculated structure factors are given in Tables 4 and 5.

Discussion

The stereoconfiguration for the *cis*-thymine glycol (I) is illustrated in Fig. 1. Bond distances and angles are shown in Fig. 2. The six-membered ring has a half-chair conformation with atoms N(1), C(2), N(3) and C(4)planar to within ± 0.05 Å, C(6) and C(5) having an average deviation of 0.37 Å from this plane. The methyl group on C(5) and the hydroxyl group on C(6) are axial to the ring while the hydroxyl group on C(5) is equatorial to the ring. The hydroxyl groups are gauche with respect to each other (pertinent torsion angles are listed in Table 6). The overall configuration of the cisthymine glycol molecule is the same as that found for ring III in the thymine trimer (Flippen & Karle, 1971) and ring I in the thymine-thymine adduct (Karle, 1969). Values for comparable bond lengths and angles also agree quite well among the three molecules. The molecular packing of (I) is dominated by an extensive network of intermolecular hydrogen bonding which involves all available hydrogen atoms (see Fig. 3). Each molecule participates in seven hydrogen bonds, four of which are independent. The hydrogen bond distances are listed in Table 7. The hydroxyl group on C(5) acts as both an acceptor and a donor while N(1), N(3) and the hydroxyl group on C(6) are donors only. Of the

Table 5. Observed and calculated structure factors for trans-1-carbamylimidazolidone-4,5-diol (II) The columns are the index k, 10|F_o|, and 10 F_c.

615	0 K	5	12 42	38	9 19 18	5 89	92	6 15	18	4 74	74	9 63	67
334	1 277	305	1 K	2	1 8 6	6 24	14	2 K	7	5 91	87	10 272	221
232	2 168	205	0 30	29	0 195 182	7 170	169	0 32	31	6 258	267	11 18	۰
66	3 16	17	1 219	207	1 156 151	8 76	73	1 70	65	7 75	75	4 K	1
61	4 35	34	2 457	423	2 54 61	9 205	205	2 82	93	8 117	115	0 249	249
244	. 120	118	3 8.5	82	3 74 74	10 118	115	3 6	0	9 75	77	1 248	246
100	á *70	***	4 192	202	4 115 110	11 28	26	1 533	552	10 100	0.8	2 324	307
	7				5 176 181			2 482	516	3 8	4	3 207	193
33	8 99	108	4 54	57	6 62 69	0 73	76	3 593	615	0 49	47	4 239	234
	0 23	24	7 46	42	7 69 68	1 68	50	4 177	169	1 197	163	5 265	264
			4 241	241		2 443	417	5 24	24	2 40	33	6 94	94
	a 21.7	71.0			A 84 49	3 30	2.	A 75	80	3 . 31	131	7 147	153
	1 121	112	10 31	31	1 96 101	4 275	263	7 160	175	4 123	124	8 50	50
9.6.2	5 62			30	2 20 19	5 176	193	8 134	142	5 25	12	9 41	41
						A 247	243	9 43		6 86	61	10 83	81
6.15			A 177	1 87	· · · ·	7 129	132	10 14	10	7 12	18	11 100	101
44.7		2.	1 102	383	0 123 119	8 216	213	11 136	138	8 102	0.8	4 6	2
	1 11		2 212	194	1 876 1054	9 70		12 7	- 3	9 64	66	0 113	
	7 41		3 201	107	2 222 233	10 141	139		· · ·	5 8		1 303	277
100	· · · ·		1 1 1	1.6	3 00 04	11 21	24	0 428		0 310	705	2 124	115
- 22		í.		. 24					304		88	3 170	154
	3			107	5 269 974	0 43	- ie	2 245	234	2 90	07	4 376	319
26	· · · ·	***	7 244	214	6 30 24	1 48	- 46	3 162	144	3 130	128	5 172	17.5
208		ັ		117	7 1 1 2 1 4	2 00		4 228	226		101	6 27	2.
	1 138	138	0 141	136	A 72 72	3 121	110	5 184	173	5 120	123	7 190	198
1	3 344	245	10 134	128	0 41 44	4 142	124	6 92	04	6 41	44	8 260	252
20		• • • •		105	10 132 131			7 62	84	7 47	42	0 54	54
2.4	4 120	130			11 40 22	6 93	94	8 105	109	8 30	37	10 70	69
512	1 1 9 4	101			12 22 20	7 56	53	9 80	83	S K	ā	11 92	91
103	6 231	226	1 117	121	2 6 1	8 151	148	10 90	50	0 7	10	4 6	3
58	7 144	145	2 65	56	0 479 496	9 19	19	11 27	22	1 134	130	0 233	221
24		1.1		148	1 15 14	10 30	39	3 8		2 44	36	1 334	316
183	9 21	21	4 103	199	2 052 043	2 6	š	0 377	367	3 157	160	2 119	104
28	10 79	82		82	3 140 131	0 269	263	1 113	90	6 28	24	3 72	71
248		10	A		4 147 141	1 208	215	2 360	350	5 28	24	4 141	135
					5 206 304	2 135	- 114	3 201	200	A 41	42	5 13	52
1				- 31	A 149 141	3 151	152	4 224	224	3 8		6 126	131
	1 203	-4.	ă 18		7 137 14		100	5 41		0 40	43	7 83	
		114							20	1 22	22		2.2
**;	2 1 1	154	10, 37		0 70	6 93	100	7 120	133			9 44	40
	1 200	104	1 4 A	5.	10 16 17	7 100	102	à 143	177	0 454	444	10 72	70
1	. 470				** ** **			÷ 103					

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two carbonyl oxygens, O(4) is the acceptor in one hydrogen bond and O(2) in two. Except for the hydrogen bond approaches there are no intermolecular contacts less than van der Waals distances.

The stereoconfiguration of the imidazolidone (II) is illustrated in Fig. 4. Bond distances and angles are shown in Fig. 5. Except for the hydroxyl groups the molecule is planar to within ± 0.23 Å. The five-membered ring is a fairly flattened envelope with atoms

N(1)-C(2)-N(3) and C(4) planar to within ± 0.03 Å, C(5) being 0.22 Å from the plane. The plane of the amide group is at an angle of 13.3° to the best plane through the five-membered ring. The hydroxyl groups are approximately *trans* to one another. The carbonyl oxygen of the amide group is oriented so that the C=O bond is *synplanar* with respect to the C(5)-N(1) bond which is the preferred orientation for such a grouping (Dunitz, 1968). As in the thymine



Fig. 3. A projection down c showing the packing in the unit cell for (I). The hydrogen bonds are shown as dotted lines.



Fig. 4. Stereodiagram of a molecule of trans-1-carbamoylimidazolidone-4,5-diol (II).

glycol the molecular packing of (II) is dominated by an intricate network of hydrogen bonding involving the 5 available hydrogen atoms in 10 hydrogen bonds per molecule (see Fig. 6). Both carbonyl oxygen atoms are acceptors in two hydrogen bonds and both hydroxyl oxygens are donors in one and acceptors in a second hydrogen bond. The ring nitrogen atom is the donor in one hydrogen bond while the amide nitrogen parti-



Fig. 5. Bond distances and angles for (II).

cipates in two hydrogen bonds, one of which is bifurcated. The bifurcated hydrogen bond has one intramolecular approach, N(6) \cdots O(2) at 2.720 Å, and one intermolecular approach, N(6) $\cdot \cdot \cdot$ O(4) at 2.985 Å. The hydrogen atom was found to lie approximately along the bisector of the $O(2) \cdots N(6) \cdots O(4)$ angle. An interesting feature of the molecule is the apparently strong electrostatic attraction between the ring C=O groups which are arranged in an anti-parallel fashion as shown in Fig. 7 with a $C(2) \cdots C(2')$ separation of only 3.16 Å. A similar arrangement of C=O groups was noted by Przybylska (1972) in a tetracyclic diketone. However, in that case the closest approach of 3.18 Å was between a carbon atom of one $\overline{C=O}$ and the oxygen atom of C=O in an adjacent molecule. The attraction between the C=O groups, as well as the extensive hydrogen bonding which links the molecules in all directions, allow the molecules to pack quite closely together and explain, in part, the relatively high crystal density of 1.71 g cm^{-3} .

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4.5

16.4

	Table 6. To	orsion angles	
Ring torsions		(II)	
$\begin{array}{c} (C_{0}-N(1)-C(2)-N(3)\\ N(1)-C(2)-N(3)-C(4)\\ C(2)-N(3)-C(4)-C(5)\\ N(3)-C(4)-C(5)-C(6)\\ C(4)-C(5)-C(6)-N(1)\\ C(5)-C(6)-N(1)-C(2)\\ \end{array}$	-6.8° -11.3 -8.6 41.8 -55.8 41.6	$\begin{array}{c} C(5)-N(1)-C(2)-N(3)\\ N(1)-C(2)-N(3)-C(4)\\ C(2)-N(3)-C(4)-C(5)\\ N(3)-C(4)-C(5)-N(1)\\ C(4)-C(5)-N(1)-C(2) \end{array}$	- 3.9 - 6.5 13.3 - 14.1 11.6
Torsional angles involvin O(6)-C(6)-C(5)-O(5) O(6)-C(6)-C(5)-C(7)	ng substituent a - 55·2° - 174·2	toms O(4)-C(4)-C(5)-O(5) O(5)-C(5)-N(1)-C(6) O(2)-C(2)-N(1)-C(6)	131·9 79·6 15·2

Table 7. Hydrogen-bond lengths

Donor	Acceptor	Distance (Å) (I)	Symmetry operation on acceptor
N(1)	O(2)	2.996	$\frac{1}{2} - x, \bar{y}, -\frac{1}{2} + z$
N(3)	O(5)	3.061	x, y, -1+z
O(5)	O(2)	2.835	$\frac{1}{2} + x$, $\frac{1}{2} - y$, $1 - z$
O(6)	O(4)	2.988	$1-x, -\frac{1}{2}+y, \frac{1}{2}-z$
		(II)	
N(3)	O(6)	2.882	$1-x, -\frac{1}{2}+y, \frac{1}{2}-z$
N(6)	O(2)	2.720	x, y, z hifurcated
N(6)	O(4)	2.985	$\frac{1}{2}+x, y, \frac{1}{2}-z$ for uncalled
N(6)	O(5)	3.008	$\frac{1}{2} + x, \frac{1}{2} - y, \bar{z}$
O(4)	O(6)	2.827	$x, \frac{1}{2}-y, \frac{1}{2}+z$
O(5)	O(2)	2 ·789	$1-x, \bar{y}, \bar{z}$

C(5)-N(1)-C(6)-O(6)

C(2)-N(1)-C(6)-N(6)



Fig. 6. A projection down c showing the packing in the unit cell for (II). The hydrogen bonds are shown as dotted lines. The hydrogen atom participating in the bifurcated hydrogen bonding is also illustrated at its refined position.



Fig. 7. Parallel arrangement of carbamoyl groups in crystal of (II).

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