Acta Cryst. (1970). B**26**, 303

The Crystal Structure and Absolute Configuration of 2′-Deoxycytidine Hydrochloride*

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(*Received* 31 *December* 1968)

2′-Deoxycytidine hydrochloride ($C_9H_{14}N_3O_4Cl$) was crystallized from water as monoclinic needles, space group $P2_1$, with $a=6\cdot561$, $b=17\cdot659$, $c=5\cdot125$ Å, $\beta=108\cdot08°$ and two molecules per cell. The crystal structure has been determined by a three-dimensional X-ray diffraction analysis. A complete hemisphere of data (positive and negative values of both h and k) was collected with a General Electric XRD-5 automatic diffractometer and nickel-filtered Cu $K\alpha$ radiation. The structure was solved by the heavy-atom method. Full-matrix least-squares refinement of both the D and L enantiomorphs has led to respective R values of 0·035 and 0·061; the configuration that gave the lower R value confirms previous conclusions regarding the absolute configuration of the D sugar. The atoms in the pyrimidine ring exhibit small but significant deviations from planarity. The torsion angle describing the conformation about the glycosidic bond is 0°. The least-squares planes through any four ring atoms of the sugar residue, normally used to describe its conformation, are unsatisfactory in that the deviations of the atoms from the planes are rather large. The conformation can, perhaps, be best described relative to the plane through C(1′), C(4′), and O(1′), with respect to which C(3′) is displaced *endo* by 0·361 Å and C(2′) is 0·245 Å *exo*.

Introduction

Accurate molecular parameters as well as the nature of the hydrogen-bonding and packing systems in nucleosides and nucleotides provide useful information toward deducing the detailed structures of the nucleic acids. We have determined the crystal structure and absolute configuration of 2′-deoxycytidine hydrochloride ($C_9H_{14}N_3O_4Cl$) as one in a series of nucleic acid constituents being studied in these laboratories.

Experimental

2′-Deoxycytidine hydrochloride (1-β-2′-deoxy-D-ribofuranosylcytosine hydrochloride) was purchased from Mann Research Laboratories Inc., New York. The compound, prepared from salmon sperm deoxyribonucleic acid (DNA) by enzymatic hydrolysis and ion-exchange purification,§ was recrystallized from water as colourless, monoclinic needles elongated along the c axis. Crystal data are shown in Table 1. The space group was determined as either $P2_1$ or $P2_1/m$ from Weissenberg photographs taken about the b and c axes and exhibiting systematic absences only amongst $0k0$ for $k=2n+1$. That the molecule lacks a centre of symmetry and $Z=2$ establishes the space group as $P2_1$. The unit-cell parameters were obtained from a least-squares procedure minimizing $\Sigma w_n(\sin^2\theta_{\rm obs}-\sin^2\theta_{\rm calc})^2(4/\lambda_n^2)$. Values of 2θ (either α_1 or α_2 reflections) for fourteen reflections were measured on a diffractometer and assigned weights, w_n, proportional to $1/\sin^2 2\theta$. The confidence limits cited are subjective, being approximately three times the estimated standard deviations obtained from the least-squares procedure.

Table 1. *Crystal data*

$a=6\cdot561\pm0\cdot001$ Å
$b=17\cdot659\pm0\cdot003$
$c=5\cdot125\pm0\cdot001$
$\beta=108\cdot08\pm0\cdot02°$
$t=27\pm3$°C

Formula: $C_9H_{13}N_3O_4.HCl$
M.W. 263·5
$\varrho_m=1\cdot548$ g.cm^{-3} (by flotation)
$\varrho_c=1\cdot551$ g.cm^{-3}
$F(000)=276$
$Z=2$
λ(Cu $K\alpha_1$) = 1·54050 Å
λ(Cu $K\alpha_2$) = 1·54434

Intensity data were measured on a General Electric XRD-5 automatic diffractometer with nickel-filtered Cu $K\alpha$ radiation and a θ–2θ scanning technique. The crystal was a square prism of dimensions 0·10 × 0·10 × 0·13 mm, sliced from a longer needle. A scanning speed of 1° per minute was employed and the scan range varied from 2° at $2\theta=20°$ to 4° at $2\theta=120°$. Background was measured for thirty seconds at the beginning and end of each scan. As a check on the sta-

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* Contribution No. 3607 from the A. A. Noyes Laboratory of Chemical Physics. This work was supported in part by research grant No. HE-02143 from the National Heart Institute, U.S. Public Health Service to the California Institute of Technology.

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§ Private communication with Mann Research Laboratories, 1969.

bility of the crystal and the instrument, the 250 reflection was remeasured every fifteen reflections: no significant variation in its intensity was noted. Two quadrants of data (positive and negative values of both *h* and *k*) totalling 2382 reflections were measured, corresponding to approximately 96% of the total theoretically possible within the copper sphere. The intensities of 31 reflections turned out to be negative and were set to zero. Each intensity was assigned a variance derived from counting statistics with an additional term ($0{\cdot}0004S^2$, where S is the scan count) to allow for systematic errors.

The intensities and their standard deviations were corrected for Lorentz and polarization factors and placed on an absolute scale by the method of Wilson (1942). The calculated value of the mass absorption coefficient (μCu $K\alpha$) is 31 cm^{-1} leading to values of μR of the order of 0·3 for the crystal used for data collection. Thus, absorption corrections were deemed unnecessary.

Structure determination and refinement

The coordinates of the chloride ion were determined from a three-dimensional, sharpened Patterson function. Four Fourier iterations led to a complete trial structure and an R value $(\Sigma|k|F_o|-|F_c||/\Sigma k|F_o|)$ of 0·23. All calculations were performed on an IBM 7094 computer using sub-programs operating under the *CRYRM* crystallographic system (Duchamp, 1964).

Initial refinement was carried out using a full-matrix, least-squares routine on positional and individual isotropic temperature parameters and a scale factor. The quantity minimized was $\Sigma w(|F_o|^2-1/k^2(|F_c|^2)^2$, k being the scale factor and w equal to $1/\sigma^2(|F_o|^2)$. Only one quadrant of data (k and l positive) was used in these early stages and no correction for anomalous scattering was applied to the scattering factor of the chloride ion. Scattering factors were taken from *International Tables for X-ray Crystallography* (1962). When the R value had been reduced to 0·078, difference Fourier syntheses were calculated in the planes where hydrogen atoms were expected to lie. Peaks ranging in height from 0·2 to 0·5 e.Å^{-3} were observed for all fourteen hydrogen atoms. These atoms were included in subsequent structure factor calculations with isotropic temperature factors of 3·0 Å^2, but their coordinates were not refined. Scattering factors used for the hydrogen atoms were those calculated by Stewart, Davidson & Simpson (1965). Refinement was continued with anisotropic temperature factors applied to the non-hydrogen atoms; when parameter shifts were less than one quarter of their e.s.d.'s, positional and isotropic thermal parameters for only the hydrogen atoms were refined.

After four cycles of hydrogen-atom refinement both the D and L enantiomorphs were dealt with separately, applying real and imaginary anomalous dispersion corrections of 0·3*e* and 0·7*e* respectively to the scattering factor for chlorine (*International Tables for X-ray Crystallography*, 1962), and including the complete data set (k both positive and negative). For space group $P2_1$ with one or more anomalous scatterers, $F_{hkl}\neq F_{h\bar{k}l}$. Refinement was then continued alternately on heavy-atom coordinates with anisotropic temperature factors, and hydrogen-atom coordinates with isotropic temperature factors, until all parameter shifts were less than one tenth of their e.s.d.'s for both enantiomorphs.

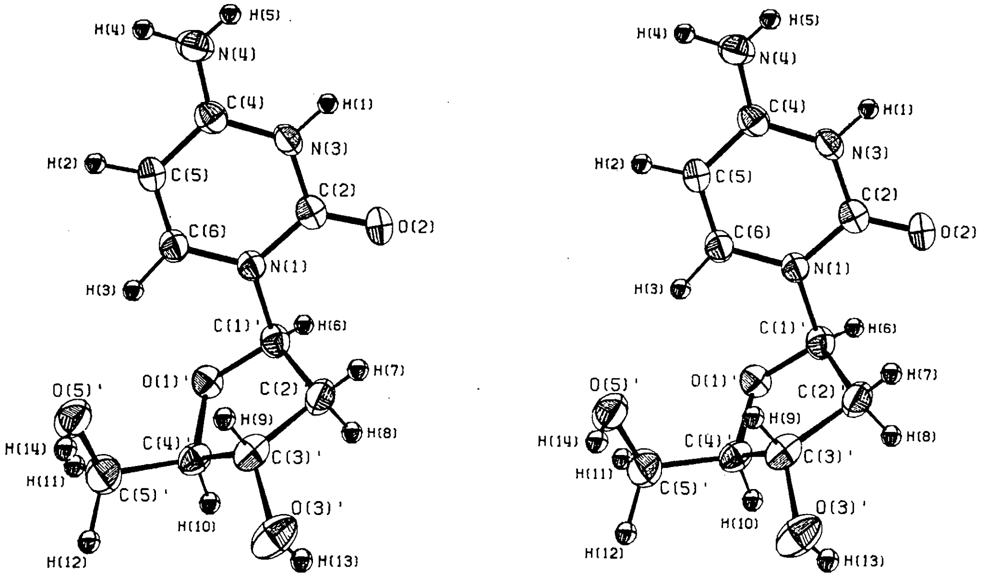

Fig. 1. A stereoscopic view of the 2′-deoxycytidine cation. The heavy atoms are represented by ellipsoids (drawn at the 50% probability level) defined by the principal axes of thermal motion.

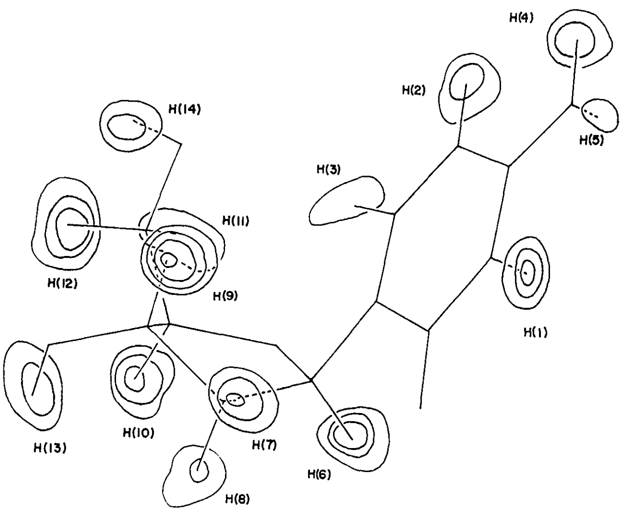

Fig. 2. The composite difference electron-density map, for which the contributions of the hydrogen atoms were excluded from the calculated structure factors. Contours are drawn at intervals of 0·1 e.Å^{-3} starting at 0·2 e.Å^{-3}.

Results and discussion

The absolute configuration of the molecule

In Table 2 are listed the final R values and the 'goodness of fit' for the D and L enantiomorphs; the agreement is conclusively better for the D enantiomorph. A stereoscopic view of the deoxycytidine cation is shown in Fig. 1, for which the *ORTEP* program was used (Johnson, 1965). This configuration for the D sugar is in agreement with previous conclusions as to its absolute configuration.

Table 2. *The final R values and 'goodness of fit' for both enantiomorphs*

	D	L
$R=(\Sigma\|k\|F_o\|-\|F_c\|\|)/\Sigma k\|F_o\|$	0·035	0·061
$[\Sigma w(k^2\|F_o\|^2-\|F_c\|^2)^2]/\Sigma w\|F_o\|^4$	0·003	0·013
'Goodness of fit' $=\left[\frac{\Sigma w(\|F_o\|^2-\|F_c\|^2/k^2)^2}{m-s}\right]^{1/2}$	1·31	2·62

In Table 3 are listed the final atomic parameters together with their e. s. d.'s for the non-hydrogen atoms;

Table 3. *The final positional and thermal parameters and their e.s.d.'s for the heavy atoms*

The temperature factors are in the form

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

All values have been multiplied by 10^5.

	x	y	z	b_{11}	b_{22}	b_{33}	b_{12}	b_{13}	b_{23}
N(1)	65477 (24)	56324 (10)	13943 (36)	1296 (40)	169 (5)	2406 (80)	−77 (24)	701 (95)	−52 (34)
C(2)	76371 (32)	60340 (12)	37243 (46)	1616 (52)	207 (7)	2327 (92)	−173 (31)	946 (118)	24 (43)
N(3)	63697 (25)	65067 (10)	47324 (36)	1624 (45)	179 (5)	2154 (79)	−168 (25)	281 (99)	−190 (34)
C(4)	42444 (31)	66316 (11)	35179 (44)	1736 (52)	164 (6)	2755 (97)	−186 (29)	1327 (119)	44 (42)
C(5)	32530 (30)	62368 (13)	10539 (48)	1241 (49)	232 (7)	3286 (103)	−117 (30)	437 (117)	−352 (47)
C(6)	44134 (29)	57536 (12)	00837 (44)	1397 (48)	190 (6)	2802 (98)	−119 (29)	638 (118)	−59 (45)
O(2)	95523 (21)	59770 (9)	48607 (35)	1369 (37)	290 (5)	3419 (75)	−105 (23)	−147 (93)	−281 (34)
N(4)	32145 (28)	71005 (10)	46346 (41)	2128 (51)	230 (6)	3408 (94)	−97 (30)	2034 (115)	−460 (40)
C(1′)	78957 (30)	51335 (12)	01950 (46)	1391 (48)	227 (7)	2577 (98)	−104 (30)	1156 (116)	−78 (44)
C(2′)	88022 (32)	44614 (14)	19966 (46)	1485 (48)	265 (7)	2705 (98)	329 (31)	507 (118)	1 (47)
C(3′)	70407 (33)	38752 (13)	09416 (45)	1734 (53)	224 (7)	2422 (95)	299 (30)	1705 (117)	243 (43)
C(4′)	62750 (30)	40361 (12)	−21163 (42)	1561 (49)	194 (7)	2314 (92)	174 (29)	1498 (111)	38 (42)
C(5′)	39631 (35)	38365 (13)	−36182 (50)	1851 (61)	276 (8)	3377 (117)	−107 (35)	1538 (136)	−338 (51)
O(1′)	65792 (22)	48502 (9)	−23247 (29)	1782 (37)	194 (4)	1967 (64)	−73 (22)	1023 (81)	107 (29)
O(3′)	76293 (24)	31115 (9)	16086 (35)	2406 (46)	248 (5)	4439 (91)	446 (26)	3124 (107)	833 (37)
O(5′)	25471 (22)	40940 (9)	−21958 (35)	1553 (38)	236 (5)	4303 (89)	97 (23)	1932 (98)	174 (37)
Cl$^-$	83510 (7)	75000	99685 (11)	1866 (13)	236 (2)	3161 (25)	−80 (9)	1175 (30)	−264 (13)

Table 4. *Final positional and thermal parameters and their e.s.d.'s for the hydrogen atoms*

The coordinates have been multiplied by 10^4.

	x	y	z	B
H(1)	7090 (32)	6782 (11)	6249 (48)	3·0 (0·5)
H(2)	1749 (35)	6289 (15)	0078 (53)	5·1 (0·6)
H(3)	3798 (37)	5446 (13)	−1789 (53)	4·3 (0·6)
H(4)	1749 (39)	7141 (15)	4051 (57)	6·1 (0·7)
H(5)	3800 (30)	7311 (11)	6065 (44)	2·9 (0·5)
H(6)	9000 (34)	5463 (13)	−0147 (52)	3·7 (0·5)
H(7)	9241 (33)	4561 (12)	3982 (48)	3·8 (0·5)
H(8)	10108 (33)	4281 (12)	1519 (47)	3·6 (0·5)
H(9)	5875 (27)	4001 (11)	1764 (38)	1·9 (0·4)
H(10)	7147 (29)	3771 (11)	−3013 (41)	2·5 (0·4)
H(11)	3561 (33)	4062 (13)	−5588 (47)	3·9 (0·5)
H(12)	3828 (30)	3240 (12)	−3902 (47)	3·4 (0·5)
H(13)	8600 (37)	3000 (15)	1353 (54)	5·1 (0·6)
H(14)	2274 (39)	3718 (14)	−1455 (56)	5·4 (0·7)

Table 5. *Final observed and calculated structure factors*

The columns are k, $10|F_o|$, $|10\sigma(|F_c|)$, $10|F_o|$, and the phase angle in degrees. The notation --- for $|F_o|$ means that $|F_o|$ was assigned the value zero; ** for the standard deviation indicates that the reflection was not included in the least-squares refinement.

	0	K	0	
-22	82	2	82	168
-20	103	2	104	331
-18	40	4	32	147
-16	76	2	72	336
-14	133	2	131	201
-12	285	3	281	49
-10	103	2	102	9
-8	202	2	201	347
-6	433	5	442	182
-4	269	5	265	150
-2	153	2	154	290
2	137	2	128	66
4	258	3	253	205
6	431	5	442	182
8	210	2	208	20
10	111	2	108	340
12	271	3	266	314
14	130	2	126	166
16	81	2	79	34
18	37	4	41	228
20	107	2	110	34
22	83	2	84	198
	1	K	0	
-22	36	2	36	311
-21	72	1	71	39
-20	59	2	58	22
-19	81	2	82	162
-18	50	2	48	174
-17	54	2	57	92
-16	52	2	50	30
-15	34	3	30	189
-14	123	2	120	208
-13	147	2	145	351
-12	210	2	205	279
-11	264	2	280	163
-10	150	1	148	247
-9	152	1	152	348
-8	179	2	179	72
-7	339	3	346	165
-6	278	2	277	134
-5	268	2	267	30
-4	316	2	325	339
-3	171	1	172	91
-2	132	1	134	156
-1	424	3	440	79
0	279	2	285	179
1	400	3	417	101
2	138	1	141	209
3	190	2	195	89
4	318	2	330	23
5	257	2	257	154
6	286	2	286	227
7	342	3	351	18
8	169	1	168	289
9	157	1	157	199
10	139	1	138	115
11	268	2	266	20
12	219	2	215	81
13	151	2	149	195
14	119	2	117	156
15	31	3	31	18
16	46	2	46	339
17	48	2	48	137
18	55	2	49	196
19	85	2	85	25
20	57	2	56	344
21	68	1	66	146
22	33	2	33	44
	2	K	0	
-21	43	2	42	328
-20	91	2	92	137
-19	36	2	36	190
-18	39	3	38	12
-17	72	2	73	28
-16	67	2	65	283
-15	19	5	12	262
-14	86	2	85	319
-13	223	2	222	346
-12	82	2	83	261
-11	58	2	56	336
-10	188	2	189	123
-9	106	1	108	15
-8	151	1	152	143
-7	299	2	299	205
-6	50	1	51	36
-5	207	2	209	1
-4	118	1	117	206
-3	217	3	219	219
-2	236	2	234	302
-1	326	2	327	14
0	542	4	562	181
1	318	2	322	170
2	249	2	246	60
3	206	2	206	326
4	113	1	112	160
5	204	2	210	185
6	47	1	47	335
7	290	2	291	338
8	156	1	158	228
9	105	1	105	178
10	158	2	157	236
11	91	2	92	187
12	73	2	76	99
13	228	2	226	198
14	92	2	90	43
15	20	8	3	47
16	64	2	65	183
17	69	2	69	160
18	43	2	37	357
19	34	3	35	6
20	54	2	55	226
21	58	1	47	220
	3	K	0	
-20	37	2	36	179
-19	13	5	15	100
-18	76	2	78	29
-17	59	2	56	294
-16	88	2	86	175
-15	73	2	72	196
-14	133	2	136	44
-13	82	2	80	143
-12	170	2	170	140
-11	69	2	67	331
-10	193	2	192	19
-9	31	3	23	6
-8	54	2	52	178
-7	76	1	75	269
-6	101	1	104	342
-5	177	2	178	224
-4	307	2	304	144
-3	175	2	174	146
-2	248	2	248	339
-1	39	2	39	32
0	193	2	187	356
1	62	2	59	149
2	236	2	237	26
3	174	2	174	34
4	312	3	311	198
5	177	2	178	315
6	111	1	112	29
7	75	1	74	272
8	56	2	56	206
9	26	3	23	176
10	189	2	187	346
11	70	2	66	209
12	183	2	181	224
13	78	2	79	37
14	127	2	127	321
15	72	2	72	345
16	89	2	88	193
17	59	2	56	246
18	74	2	76	343
19	20	3	26	79
20	37	2	37	195
	4	K	0	
-19	18	3	19	90
-18	8	6	9	164
-17	62	2	62	173
-16	49	2	47	157
-15	68	2	69	342
-14	21	4	18	238
-13	59	2	59	150
-12	70	2	72	256
-11	88	2	89	164
-10	161	2	160	338
-9	186	2	188	145
-8	66	2	67	174
-7	122	2	119	2
-6	34	3	32	61
-5	351	2	351	228
-4	133	2	131	233
-3	172	2	167	6
-2	57	2	54	57
-1	168	2	167	120
0	142	1	141	182
1	181	2	181	55
2	50	2	45	311
3	170	2	166	180
4	146	1	143	130
5	139	2	139	316
6	22	4	24	312
7	120	2	120	186
8	71	2	69	194
9	183	2	185	349
10	185	2	184	24
11	83	2	86	8
12	67	2	65	106
13	67	2	66	39
14	88	3	84	112
15	74	2	72	206
16	91	2	80	209
17	64	2	63	15
18	17	4	9	162
19	24	2	14	198
	5	K	0	
-17	60	1	61	174
-16	11	5	4	163
-15	59	2	63	349
-14	60	2	63	229
-13	110	2	111	277
-12	103	2	103	1
-11	180	2	180	4
-10	31	3	17	126
-9	119	2	117	132
-8	70	2	70	315
-7	24	4	31	154
-6	29	3	22	246
-5	45	2	44	167
-4	50	2	47	288
-3	182	2	181	340
-2	45	2	46	199
-1	110	2	114	231
0	83	2	79	3
1	103	2	103	315
2	48	2	44	170
3	188	2	187	204
4	54	2	54	75
5	54	2	50	30
6	---	**	16	123
7	29	3	28	359
8	74	2	75	49
9	127	2	128	32
10	31	3	22	245
11	181	2	180	180
12	102	2	103	2
13	102	2	101	263
14	56	2	59	136
15	68	1	65	199
16	18	3	5	142
17	63	1	63	13
	6	K	0	
-14	52	1	51	87
-13	52	1	53	113
-12	31	2	28	63
-11	63	2	61	86
-10	88	2	89	186
-9	20	4	15	59
-8	97	2	100	25
-7	22	4	18	180
-6	49	2	43	194
-5	20	5	11	280
-4	126	2	128	6
-3	90	2	90	352
-2	84	2	87	223
-1	104	2	109	51
0	64	2	62	7
1	106	2	110	129
2	79	2	78	145
3	100	2	100	188
4	125	2	127	0
5	14	6	10	260
6	47	2	42	183
7	20	3	17	357
8	97	2	96	342
9	22	4	15	118
10	88	2	88	181
11	63	2	60	95
12	28	3	19	312
13	54	1	54	67
14	58	1	60	273
	7	K	0	
-10	49	1	49	157
-9	26	2	25	38
-8	---	**	5	349
-7	9	6	11	101
-6	56	2	54	202
-5	73	2	72	345
-4	34	3	37	68
-3	69	2	68	160
-2	69	2	67	157
-1	24	4	26	35
0	19	4	13	166
1	20	4	22	168
2	65	2	70	208
3	72	2	71	26
4	31	3	31	296
5	73	2	79	202
6	54	2	52	164
7	27	3	19	84
8	15	4	9	50
9	19	3	21	158
10	91	1	91	208
	-8	K	1	
-4	---	**	9	299
-3	34	2	32	30
-2	17	4	10	220
-1	45	2	46	148
0	37	2	36	183
1	52	2	51	40
2	17	4	13	127
3	21	4	29	164
4	15	4	7	46
	-7	K	1	
-11	44	2	44	5
-10	16	5	9	235
-9	42	2	39	198
-8	50	3	50	37
-7	---	**	22	264
-6	87	2	87	146
-5	47	3	48	245
-4	61	3	39	126
-3	125	2	125	354
-2	35	4	30	168
-1	71	3	49	179
0	114	2	115	2
1	54	3	50	12
2	30	5	32	204
3	126	2	126	190
4	30	4	34	228
5	44	3	39	300
6	91	2	91	217
7	18	6	20	274
8	47	3	47	329
9	39	3	37	354
10	---	**	5	162
11	44	2	44	184
	-6	K	1	
-15	50	2	53	282
-14	76	2	79	167
-13	51	2	50	346
-12	50	3	51	350
-11	19	6	19	156
-10	61	3	63	174
-9	37	4	29	180
-8	105	2	105	352
-7	94	2	89	157
-6	111	2	109	172
-5	82	2	85	148
-4	74	2	72	48
-3	45	4	45	287
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8	33	5	33	167
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9	53	2	53	262
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9	88	2	93	153
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3	117	2	113	347
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Table 5 (*cont.*)

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2	121	2	124	45
3	116	2	117	140
4	105	2	103	239
5	107	2	107	125
6	149	2	152	343
7	29	5	21	229
8	82	2	81	221
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11	73	3	78	233
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5	206	3	202	349
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3	34	8	34	322
4	38	8	45	47

the corresponding values for the hydrogen atoms are given in Table 4. The e.s.d.'s for the L enantiomorph are about twice those listed for the D form. The corresponding atomic parameters for the two enantiomorphs did not differ, in most cases, by more than one e.s.d. of the D model (except for the sign change in the coordinates). The most significant difference was for the b_{11} term of the chloride ion, which was nearly three e.s.d.'s smaller for the L model than for the D. Table 5 is the final structure-factor list. Fig. 2 shows a composite difference Fourier synthesis for which the contributions of the hydrogen atoms were excluded from the calculated structure factors. In space group $P2_1$ with a number of anomalous scatterers, the expression for the electron density is a complex quantity. The composite difference Fourier synthesis (Fig. 2) was calculated using the real part of this quantity. An electron-density map calculated with only the imaginary terms had a peak of maximum height 2·8 e.Å^{-3} at the position of the chloride ion as its only significant feature.

Packing and hydrogen bonding

The view of the crystal structure down **c*** (Fig. 3) shows the packing arrangement, proposed hydrogen bonds (broken lines) and the hydrogen-bond distances. Some close intermolecular distances are also given. Intermolecular contacts and hydrogen-bond angles are given in Table 6. It is interesting that the amino nitro-

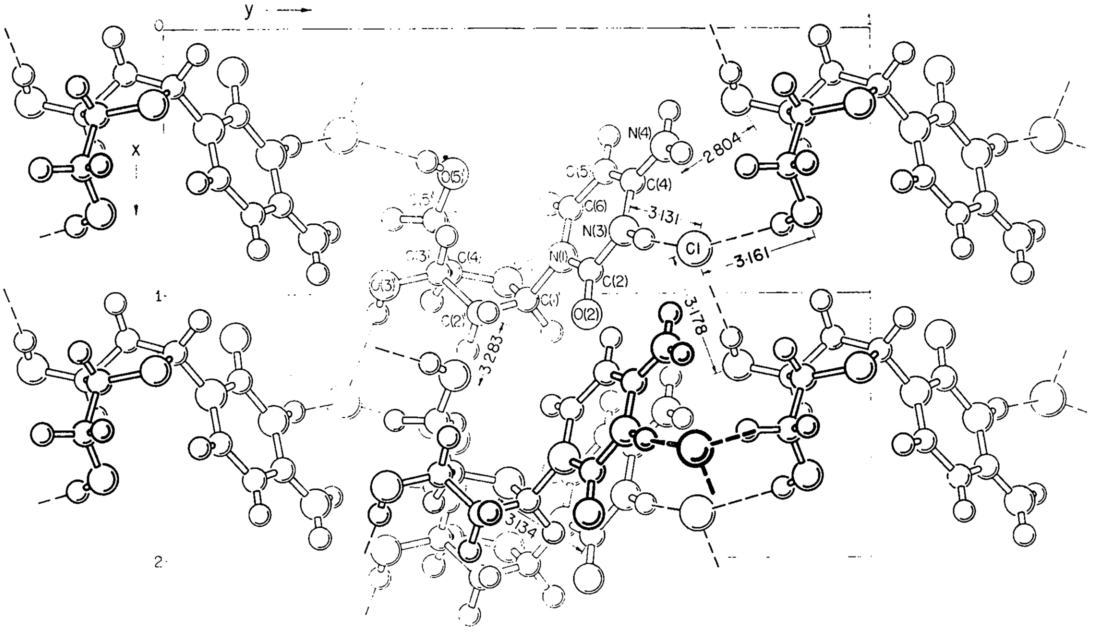

Fig. 3. The crystal structure viewed down **c***.

gen atom, N(4), forms at best only very weak hydrogen bonds. The N(4)–O(3′) $(1-x,\frac{1}{2}+y,1-z)$ distance of 2·804 Å is favourable but H(5) lies 39° from the N–O line; H(4) lies 26° from the line N(4)–Cl^- $(-1+x,y,-1+z)$ and the N–Cl^- distance is long (3·415 Å). Also, the distance N(4)–O(2) $(-1+x,y,z)$ is 3·146 Å but H(4) lies 48° from the N–O line.

Table 6. *Some intermolecular close contacts and hydrogen-bond angles*

Proposed hydrogen bond distances are identified by *.

	Distance
O(1′) (I) —N(1)	3·497 Å
O(1′) (I) —C(2)	3·134
O(1′) (I) —N(3)	3·274
O(1′) (I) —O(2)	3·405
N(4) (II)—O(2)	3·146
C(6) (III) -O(2)	3·492
O(5′) (III)-C(2′)	3·283
O(3′) (IV)-N(4)	2·804
N(3) ——Cl^-	3·131*
O(5′) (IV)-Cl^-	3·161*
O(3′) (V) -Cl^-	3·178*
N(4) (III)-Cl^-	3·415

	Angle
C(4)———N(3) ——Cl^-	113·3°
C(2)———N(3) ——Cl^-	121·3
C(5′) (IV) —O(5′) (IV)-Cl^-	97·2
C(3′) (V)—O(3′) (V)—Cl^-	116·6
C(4)———N(4) ——O(3′) (IV)	160·5
C(4) (III)—N(4) (III)-Cl^-	108·8
C(4) (II) —N(4) (II)—O(2)	97·8
H(4)———N(4) ——O(3′) (IV)	76·0
H(5)———N(4) ——O(3′) (IV)	39·0
H(14) (IV)—O(5′) (IV)-Cl^-	8·0
H(1)———N(3) ——Cl^-	6·0
H(13) (IV)—O(3′) (V)—Cl^-	6·0
H(4) (II) —N(4) (II)—O(2)	48·0
H(4) (III) —N(4) (III)-Cl^-	26·0

(I) = $x, y, 1+z$
(II) = $1+x, y, z$
(III) $1+x, y, 1+z$
(IV) = $1-x, \frac{1}{2}+y, 1-z$
(V) = $2-x, \frac{1}{2}+y, 1-z$

Each chloride ion is surrounded by two oxygen atoms [O(3′) $(2-x,\frac{1}{2}+y,1-z)$ and O(5′) $(1-x,\frac{1}{2}+y,1-z)$] and a nitrogen atom, N(3), at distances of 3·178, 3·161, and 3·131 Å respectively. In each case the distances are less than the sum of the van der Waals radii for oxygen or nitrogen and chlorine atoms (Pauling, 1960) and the hydrogen atoms are directed towards the chloride ion; the deviations from linearity are given in Table 6.

In 2′-deoxycytidine hydrochloride, as in both the orthorhombic and monoclinic crystal structures of cytidylic acid *b* (Sundaralingam & Jensen, 1965; Bugg & Marsh, 1967), the carbonyl oxygen atom, O(2), fails to participate in hydrogen bonding.

The pyrimidine rings of molecules related by one unit-cell translation in the *c* direction lie in planes approximately 3·2 Å apart, but there is very little overlap when viewed perpendicular to the planes. The

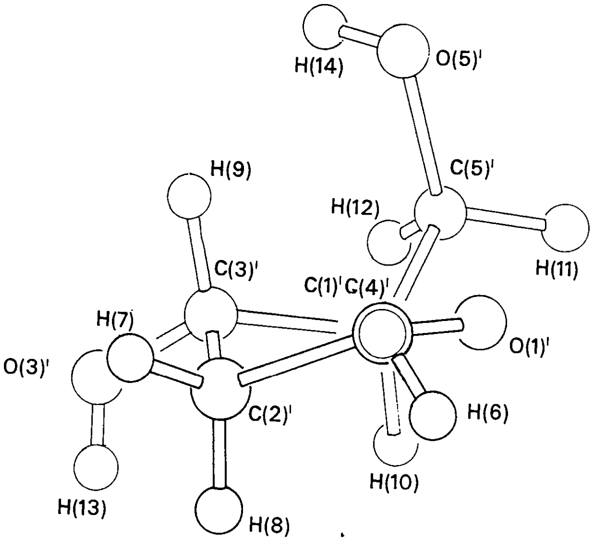

Fig. 4. The sugar residue viewed in the direction from C(1′) to C(4′).

Table 7. *Least-squares planes through the ring atoms of the sugar residue*

	Deviations (Å)					
	(*a*)	(*b*)	(*c*)	(*d*)	(*e*)	(*f*)
C(1′)	−0·050	0·052	0·172	0·137	0·313†	0·000
O(1′)	0·080	−0·054	−0·110	0·039†	0·120	0·000
C(4′)	−0·075	0·032	−0·386†	−0·137	−0·188	0·000
C(3′)	0·045	0·557†	0·098	0·219	0·181	0·361†
C(2′)	−0·541†	−0·030	−0·159	−0·220	−0·113	−0·245†
C(5′)	0·942†	0·881†	0·271†	0·698†	0·543†	0·935†

The equations of the least-squares planes, with coefficients equal to the direction cosines of the plane normal with respect to the crystallographic axes, are:

(*a*) $-0·9518X+0·2715Y+0·4306Z=-2·377$
(*b*) $-0·9519X+0·1158Y+0·6495Z=-3·919$
(*c*) $-0·8431X+0·3570Y+0·6437Z=-1·239$
(*d*) $-0·9072X+0·2905Y+0·5707Z=-2·117$
(*e*) $-0·8652X+0·3778Y+0·5817Z=-1·312$
(*f*) $-0·9427X+0·1727Y+0·5636Z=-3·262$

† Means an atom excluded from the calculation of the plane.

closest contact between the rings is 3·675 Å from C(6) $(x,y,1+z)$ to C(4). Hence, it seems that base-stacking interactions play little part in stabilizing the crystal structure.

The molecular conformation

The torsion angle (Sundaralingam & Jensen, 1965) describing the relative orientations of the sugar and base residues is 0°;* the atoms N(1), C(6), C(1′), and O(1′) lie in a plane, within the accuracy of this determination. This conformation is significantly different from those reported to date for all other pyrimidine nucleosides and nucleotides with the possible exception of the uridine residue in β-adenosine-2′-β-uridine-5′-phosphoric acid (Shefter, Barlow, Sparks & Trueblood, 1964) for which the torsion angle is reported as −5°. For all other pyrimidine nucleosides and nucleotides the range of torsion angles is from −20 to −65°. The conformation adopted in 2′-deoxycytidine hydrochloride would seem to be unfavourable sterically, in that it results in O(1′) being at its minimum possible distances from C(6) (2·679 Å) and H(3) (2·20 Å), which are respectively 0·17 and 0·15 Å smaller than the 'normal' intramolecular distances listed by Haschemeyer & Rich (1967). Usually, base-to-sugar close contacts in pyrimidine nucleosides and nucleotides are between the hydrogen atom attached to C(1′) and the atoms C(2) and O(2). In the orthorhombic and monoclinic forms of cytidylic acid *b* (Sundaralingam & Jensen, 1965; Bugg & Marsh, 1967) and in 5-fluorodeoxyuridine (Harris & MacIntyre, 1964) these H–O distances are 2·23, 2·27, and 2·19 Å respectively, not significantly different from the O(1′)–H(3) distance in 2′-deoxycytidine hydrochloride.

Table 7 shows all possible least-squares planes through four ring atoms of the sugar residue in 2′-deoxycytidine hydrochloride. Previously, for most pyrimidine nucleosides and nucleotides, the conformation of the sugar residue has been best described relative to one of these planes with either C(2′) or C(3′) significantly displaced from the plane. However, in 2′-deoxycytidine hydrochloride, the deviations of the atoms from these two planes (Table 7, planes *a*,*b*) are rather large;* thus, the conformation is perhaps best described relative to the plane through the atoms C(1′), C(4′), and O(1′). Sundaralingam (1965) also makes use of this plane in a review article on sugar conformations. With respect to this plane in 2′-deoxycytidine hydrochloride

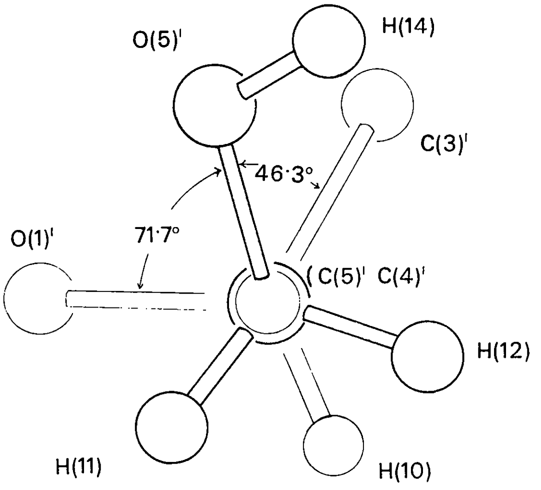

Fig. 5. The conformation of the bond C(5′)–C(4′).

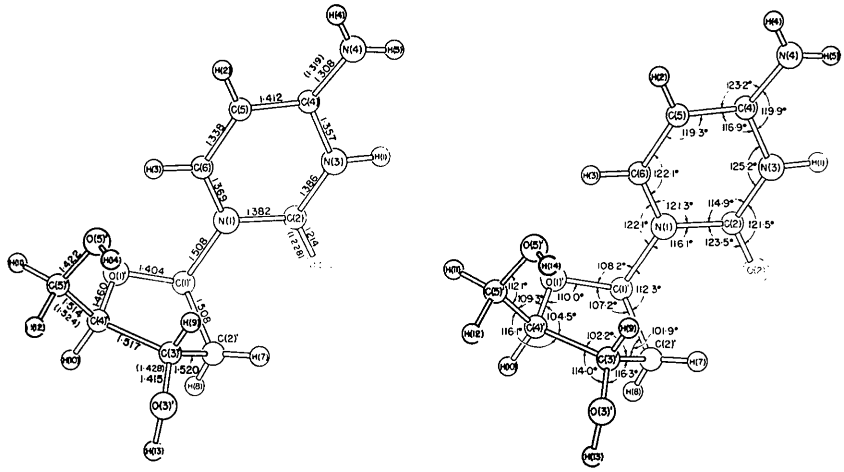

Fig. 6. Intramolecular bond distances and angles involving the heavy atoms.

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* Two other, slightly different definitions for the torsion angle are commonly used (Donohue & Trueblood, 1960; Haschemeyer & Rich, 1967), resulting in small differences in values. For example, using the definition of Haschemeyer & Rich the torsion angle for 2′-deoxycytidine hydrochloride is −3·5°.

* The root mean square deviations of the atoms from the planes excluding C(2′) and C(3′) are 0·064 and 0·043 Å respectively.

(Table 7, plane *f*), C(3′) is displaced *endo* [to the same side of the plane as C(5′)] by 0·361 Å and C(2′) is 0·245 Å *exo*. The sugar residue viewed in the direction C(1′)–C(4′) is shown in Fig. 4. The puckering of the five-membered ring can also be described by individual torsion angles for the ring bonds – the dihedral angle between the planes defined by a bond and its two adjacent ring bonds (Brown & Levy, 1963). The values for 2′-deoxycytidine hydrochloride are C(1′) → O(1′) = −9·9°, O(1′) → C(4′) = 14·2°, C(4′) → C(3′) = −31·9°, C(3′) → C(2′) = 36·9°, and C(2′) → C(1′) = −29·5°.

The conformation of the bond C(5′)–C(4′) can be seen in Fig. 5 which also shows the two projected valency angles $\varphi_{OO} = 71{\cdot}7°$ and $\varphi_{OC} = 46{\cdot}3°$ as defined by Shefter & Trueblood (1965). The conformation is *gauche-gauche*, the bond C(5′)–O(5′) being on the same side of the bonds O(1′)–C(4′) and C(3′)–C(4′). This conformation occurs most frequently in nucleosides and nucleotides.

The molecular geometry

As in cytidylic acid *b* (Sundaralingam & Jensen, 1965; Bugg & Marsh, 1967), the deoxycytidine cation is protonated at N(3). Intramolecular bond lengths and angles are shown in Fig. 6; the corresponding e.s.d.'s are 0·003 Å and 0·2° respectively. The values in parentheses in this Figure include estimated corrections for thermal motion on the basis of a riding model (Busing & Levy, 1964). However, discussion will be restricted to the uncorrected values.

The bond lengths and angles in the sugar residue agree quite well with those reported previously for other nucleosides and nucleotides and the values observed for the cytosine moiety are in very good agreement with those reported for cytidylic acid *b*. Probably the only significant difference is for the bond N(1)–C(1′), 1·508 (0·003) Å in 2′-deoxycytidine hydrochloride and 1·475 (0·006) Å in the orthorhombic form of cytidylic acid *b* and 1·485 (0·009) Å in the monoclinic form. The lengthening of the bond in 2′-deoxycytidine hydrochloride might be explained by repulsive forces between the electrons in the bonds N(1)–C(6) and C(1′)–O(1′), which lie in the same plane. In the orthorhombic and monoclinic forms of cytidylic acid *b*, the angles between the analogous bonds are about 42° and 39° respectively.

The pyrimidine ring is slightly but significantly non-planar. The deviations from the least-squares plane

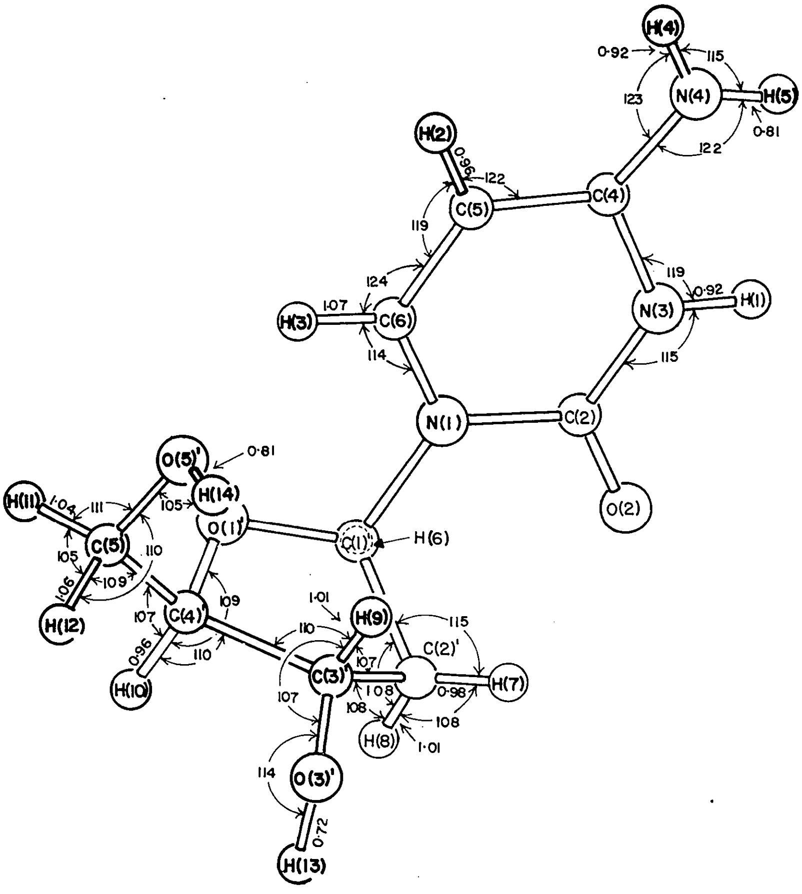

Fig. 7. Intramolecular bond distances and angles involving the hydrogen atoms. C(1′)–H(6) = 0·99 Å, N(1)–C(1′)–H(6) = 107°, O(1′)–C(1′)–H(6) = 109°, C(2′)–C(1′)–H(6) = 114°, C(3′)–C(2′)–H(7) = 116°, and C(4′)–C(5′)–H(11) = 109°.

through the six ring atoms are given in Table 8; the exocyclic atoms O(2), N(4), and C(1′) are considerably displaced from this plane.

Table 8. *The least-squares plane through the six ring atoms of the pyrimidine base*

	Deviation
N(1)	0·024 Å
C(2)	−0·029
N(3)	0·012
C(4)	0·010
C(5)	−0·015
C(6)	−0·002
O(2)	−0·086†
N(4)	0·029†
C(1′)	−0·065†
H(1)	−0·045†
H(2)	−0·009†
H(3)	−0·048†
H(4)	0·168†
H(5)	0·065†
Cl⁻	−0·105†

The equation of the least-squares plane, with coefficients equal to the direction cosines of the plane normal with respect to the crystallographic axes is

$$-0{\cdot}3993X-0{\cdot}7422Y+0{\cdot}6354Z=-8{\cdot}667\ .$$

† Means an atom excluded from the calculation of the plane.

The bond lengths and angles involving the hydrogen atoms are shown in Fig. 7; the e.s.d.'s in bond lengths and angles range respectively from 0·02 to 0·03 Å and from 1 to 2°. As is now commonly observed in X-ray diffraction investigations where electron density rather than nuclear density is examined, several bond lengths are significantly shorter than the accepted values (Pauling, 1960).

Thermal motion

It appears that the motions of all the heavy atoms are significantly anisotropic in that at least one of their b_{ij} terms (Table 3) differs by more than three e.s.d.'s from the value it would have assuming isotropic motion with B equal to the mean principal axis B_i. Although corrections to several bond lengths were estimated on the basis of a simple riding model (Busing & Levy, 1964) and are shown in Fig. 6, no attempt was made to correct bond lengths for other librational effects.

We are grateful to Dr R. E. Marsh for helpful discussion and to Mrs J. Westphal for adapting certain computer programs to deal with the anomalous dispersion effect.

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