ACTA CHEMICA SCANDINAVICA 24 (1970) 3230–3236

Crystal Structure of Pyrimidine-2-one

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The crystal structure of pyrimidine-2-one has been determined by X-ray crystallographic methods and refined to $R=0.055$. The space group is $P4_12_12$. The intensities of 518 reflections were measured on an automatic diffractometer using Mo$K\alpha$ radiation. The estimated standard deviation in bond lengths involving non-hydrogen atoms is 0.003—0.004 Å. The structure is compared with those of pyrimidine and cytosine.

Pyrimidine-2-one (2-hydroxy-pyrimidine) may be considered the parent substance of the biologically important pyrimidine bases and it would appear to be of considerable interest to know its structure. The structure of the pyrimidines of the nucleic acids,[1-3] as well as that of pyrimidine itself,[4] has been determined by X-ray crystallographic methods.

STRUCTURE DETERMINATION

A sample of pyrimidine-2-one was kindly supplied by professor S. G. Laland. Crystals were grown by evaporating an ethylacetate solution. Needles (up to 5 cm long) extended along c were obtained. The space group is $P4_12_12$ ($P4_32_12$). The unit cell dimensions were measured on a manual diffractometer and found to be $a=b=8.571\pm0.003$ Å, $c=12.406\pm0.003$ Å. Flotation gave a density of 1.37 g/cm^3. The calculated density is 1.40 g/cm^3.

A crystal of dimensions $0.28\times0.20\times0.20$ mm was used to measure the intensities on a Picker automatic diffractometer using Mo$K\alpha$ radiation ($\lambda=0.71069$ Å). The $\omega/2\theta$ scan technique (rate 2°/min) was employed. Out of the 1300 reflections with $2\theta<75°$ only 518 had intensities greater than twice the standard deviation. Absorption correction was not applied.

The structure was solved by Patterson and trial-error methods and refined by full matrix least squares to $R=0.067$. The weighting scheme was based on standard deviation from counter statistics and 2 % fluctuation in diffractometer stability. Secondary extinction correction and further refinement gave a final R-value of 0.055 ($R_w=0.034$). In Table 1 the observed and calculated structure factors are listed. The atomic parameters were then corrected for thermal effects, assuming the molecule to be rigid.[5] The root mean square

Table 1. Observed and calculated structure factors.

h	k	l	F_o	F_c
0	0	4	277	279
0	0	8	48	50
0	0	12	405	407
0	0	16	68	68
1	0	1	65	62
1	0	2	702	735
1	0	3	206	204
1	0	4	189	193
1	0	5	294	298
1	0	6	86	91
1	0	7	94	92
1	0	8	167	167
1	0	9	54	55
1	0	11	124	120
1	0	12	85	77
1	0	13	106	103
1	0	14	143	142
2	0	0	164	169
2	0	1	150	150
2	0	2	55	53
2	0	3	20	19
2	0	4	226	219
2	0	5	445	453
2	0	6	123	126
2	0	7	362	368
2	0	8	166	187
2	0	9	82	81
2	0	10	117	116
2	0	11	55	58
2	0	12	48	48
2	0	14	40	37
2	0	15	37	34
3	0	2	301	296
3	0	3	259	255
3	0	5	114	113
3	0	6	162	166
3	0	7	110	107
3	0	8	33	31
3	0	9	28	28
3	0	10	25	23
3	0	11	28	23
3	0	13	43	31
3	0	14	49	41
3	0	15	59	45
4	0	0	114	113
4	0	1	138	139
4	0	2	103	99
4	0	3	58	56
4	0	4	182	179
4	0	5	158	153
4	0	6	41	45
4	0	7	28	34
4	0	8	66	64
4	0	9	53	50
4	0	10	41	43
4	0	12	45	45
4	0	13	37	43
5	0	2	24	25
5	0	3	65	66
5	0	4	33	30
5	0	7	27	27
5	0	8	39	42
5	0	9	46	58
5	0	0	22	17
6	0	1	148	145
6	0	2	88	96
6	0	3	29	29
6	0	4	112	112
6	0	5	129	128
6	0	6	104	105
6	0	7	51	55
6	0	8	51	60
6	0	10	47	54
6	0	11	62	72
7	0	1	111	110
7	0	3	75	80
7	0	4	64	65
7	0	6	65	62
7	0	11	34	39
7	0	13	53	45
7	0	16	44	25
8	0	0	82	81
8	0	1	81	81
8	0	2	72	68
8	0	3	129	126
8	0	4	32	35
8	0	5	66	66
8	0	6	34	28
8	0	7	67	66
8	0	8	62	50
8	0	9	37	38
8	0	10	60	51
9	0	2	53	44
9	0	3	44	40
9	0	9	36	21
9	0	11	55	50
9	0	12	51	46
9	0	13	56	48
10	0	0	170	171
10	0	1	49	49
10	0	11	46	43
10	0	12	74	62
11	0	4	40	30
11	0	5	46	40
12	0	0	39	9
12	0	6	42	30
1	1	0	116	119
1	1	1	454	414
1	1	2	556	548
1	1	3	289	283
1	1	4	543	551
1	1	5	112	112
1	1	6	138	155
1	1	7	20	16
1	1	8	126	125
1	1	9	183	185
1	1	10	144	144
1	1	11	213	214
1	1	12	29	24
1	1	13	57	55
1	1	14	69	70
1	1	16	46	40
2	1	0	701	700
2	1	1	430	428
2	1	2	643	644
2	1	3	512	517
2	1	4	62	57
2	1	5	249	251
2	1	6	135	134
2	1	7	300	297
2	1	8	33	31
2	1	9	127	126
2	1	10	140	145
2	1	11	100	101
2	1	12	119	118
2	1	14	53	61
2	1	15	65	62
3	1	0	54	54
3	1	1	252	251
3	1	2	130	126
3	1	3	295	294
3	1	4	186	181
3	1	5	244	243
3	1	6	136	137
3	1	7	106	104
3	1	8	35	37
3	1	9	88	85
3	1	10	64	69
3	1	11	51	50
3	1	14	30	25
3	1	15	57	50
4	1	1	185	183
4	1	2	124	125
4	1	3	82	82
4	1	4	180	180
4	1	5	166	164
4	1	6	24	22
4	1	7	113	112
4	1	8	72	69
4	1	9	52	47
4	1	10	74	82
4	1	11	78	78
5	1	1	157	158
5	1	2	79	76
5	1	3	95	99
5	1	5	27	22
5	1	6	19	12
5	1	7	47	44
5	1	8	29	26
5	1	9	38	27
5	1	12	29	13
5	1	13	35	33
5	1	14	38	39
6	1	1	36	40
6	1	2	53	55
6	1	3	75	79
6	1	4	70	73
6	1	5	22	27
6	1	7	41	43
6	1	8	49	52
6	1	9	65	70
6	1	10	64	66
6	1	11	38	33
7	1	0	53	52
7	1	1	39	34
7	1	3	57	59
7	1	4	56	55
7	1	5	56	55
7	1	6	59	62
7	1	9	60	65
7	1	10	42	45
7	1	13	36	34
8	1	0	152	152
8	1	1	121	116
8	1	2	106	106
8	1	3	100	101
8	1	5	32	31
8	1	6	56	53
8	1	7	65	66
8	1	8	36	21
8	1	10	36	37
8	1	11	38	38
8	1	12	59	50
8	1	14	56	39
8	1	15	47	35
9	1	1	112	110
9	1	2	90	90
9	1	4	39	38
9	1	11	41	61
10	1	0	51	54
10	1	1	48	45
10	1	2	50	45
10	1	3	34	35
10	1	6	54	42
10	1	8	41	31
10	1	14	50	21
11	1	4	49	37
11	1	5	39	16
11	1	8	42	18
11	1	11	50	24
2	2	0	683	660
2	2	1	140	143
2	2	2	284	280
2	2	3	350	345
2	2	4	162	165
2	2	5	85	89
2	2	6	17	23
2	2	7	53	55
2	2	8	66	68
2	2	9	29	29
2	2	10	27	21
2	2	12	97	90
2	2	13	49	50
2	2	14	49	49
2	2	15	70	66
2	2	16	57	48
3	2	0	48	47
3	2	1	125	124
3	2	2	156	152
3	2	3	23	31
3	2	4	202	203
3	2	5	97	97
3	2	6	92	92
3	2	7	107	107
3	2	8	188	190
3	2	9	86	92
3	2	10	132	131
3	2	11	58	60
3	2	12	37	31
3	2	14	41	43
4	2	0	80	82
4	2	1	155	153
4	2	2	94	92
4	2	3	98	97
4	2	4	156	156
4	2	5	95	97
4	2	7	28	29
4	2	8	135	139
4	2	9	84	82
4	2	10	40	45
4	2	11	38	45
4	2	12	53	55
4	2	13	55	52
4	2	14	41	32
4	2	15	48	38
5	2	0	411	409
5	2	1	67	66
5	2	2	102	103
5	2	3	213	214
5	2	4	125	122
5	2	5	42	42
5	2	6	23	14
5	2	8	25	17
5	2	9	56	60
5	2	10	25	20
5	2	11	49	51
5	2	12	83	82
6	2	0	22	16
6	2	1	112	114
6	2	2	70	68
6	2	3	165	167
6	2	4	137	140
6	2	5	72	77
6	2	6	61	59
6	2	7	27	29
6	2	8	82	82
6	2	9	48	48
6	2	10	30	26
6	2	15	40	40
7	2	1	50	54
7	2	2	75	73
7	2	3	98	97
7	2	4	139	138
7	2	5	85	88
7	2	6	32	31
7	2	7	59	56
7	2	8	114	109
7	2	9	62	60
7	2	10	52	54
7	2	11	36	37
7	2	16	47	16
8	2	0	60	65
8	2	2	54	49
8	2	3	28	31
8	2	4	37	38
8	2	5	30	32
8	2	8	52	42
8	2	9	31	31
8	2	13	44	37
9	2	0	63	54
9	2	1	28	24
9	2	3	62	58
9	2	4	46	47
9	2	7	36	44
9	2	12	37	24
10	2	5	51	46
10	2	6	47	32
10	2	7	42	36
10	2	10	39	32
13	2	6	41	7
3	3	0	131	128
3	3	1	157	150
3	3	2	381	385
3	3	3	454	456
3	3	4	330	336
3	3	5	200	199
3	3	6	53	53
3	3	7	173	175
3	3	8	128	131
3	3	9	165	169
3	3	10	135	136
3	3	11	50	44
3	3	13	50	47
3	3	14	43	48
3	3	15	53	54
4	3	0	135	131
4	3	1	239	233
4	3	2	65	65
4	3	3	174	177
4	3	4	88	90
4	3	5	21	21
4	3	6	98	98
4	3	7	64	67
4	3	8	46	48
4	3	9	42	39
4	3	10	32	28
4	3	11	62	67
4	3	12	33	28
4	3	13	48	42
4	3	14	45	37
4	3	15	54	50
5	3	0	93	93
5	3	1	75	75
5	3	2	153	151
5	3	3	70	71
5	3	4	126	126
5	3	5	123	125
5	3	6	107	108
5	3	7	104	104
5	3	8	135	138
5	3	10	74	74
5	3	11	68	70
5	3	13	42	44
6	3	0	86	87
6	3	1	89	91
6	3	2	42	41
6	3	3	69	74
6	3	4	63	66
6	3	5	49	48
6	3	6	54	56
6	3	7	68	70
6	3	8	27	32
6	3	9	43	43
6	3	11	45	49
6	3	15	45	39
7	3	3	114	113
7	3	4	96	96
7	3	5	56	54
7	3	6	66	70
7	3	7	29	30
7	3	9	44	46
7	3	10	49	51
7	3	14	45	40
7	3	16	43	21
8	3	5	38	26
8	3	4	59	59
8	3	8	56	61
9	3	1	37	29
9	3	3	40	40
9	3	6	61	58
9	3	10	48	32
10	3	0	35	25

Table 1. Continued.

h	k	l	F_o	F_c	h	k	l	F_o	F_c	h	k	l	F_o	F_c	h	k	l	F_o	F_c
10	3	4	39	25	6	4	5	100	99	5	5	9	35	30	6	6	7	103	104
3	4	0	229	226	6	4	6	39	31	6	5	0	91	92	6	6	9	60	57
4	4	1	24	26	6	4	7	144	146	6	5	1	74	77	6	6	12	46	43
4	4	2	77	76	6	4	8	65	66	6	5	3	37	37	7	6	0	36	35
4	4	3	113	116	6	4	9	57	57	6	5	4	98	97	7	6	1	30	33
4	4	4	93	92	6	4	10	34	15	6	5	5	103	105	7	6	2	35	37
4	4	5	95	97	6	4	11	40	40	6	5	6	35	28	7	6	3	31	14
4	4	6	22	19	6	4	12	48	46	6	5	7	62	65	7	6	5	39	37
4	4	7	244	247	7	4	0	53	55	6	5	10	49	38	7	6	7	35	38
4	4	8	42	46	7	4	1	81	89	6	5	12	38	32	7	6	8	36	30
4	4	9	80	78	7	4	2	81	83	6	5	13	39	22	7	6	10	37	34
4	4	10	38	40	7	4	3	74	78	6	5	17	45	28	7	6	13	47	6
4	4	11	30	19	7	4	4	37	37	7	5	1	38	38	8	6	1	30	29
4	4	12	49	50	7	4	5	33	25	7	5	2	43	41	8	6	3	35	34
4	4	17	45	22	7	4	7	32	27	7	5	3	35	37	7	7	0	39	31
5	4	0	49	51	7	4	11	50	35	7	5	4	38	42	7	7	2	41	36
5	4	1	34	32	8	4	0	59	67	7	5	5	55	51	7	7	3	32	45
5	4	2	73	76	8	4	1	32	27	7	5	8	50	46	7	7	4	37	45
5	4	3	44	46	8	4	2	49	43	7	5	9	45	34	7	7	5	32	30
5	4	4	174	179	8	4	3	33	27	7	5	10	55	42	8	7	1	32	17
5	4	5	265	267	8	4	4	28	31	7	5	11	46	44	8	7	2	38	41
5	4	6	191	190	8	4	7	39	31	8	5	0	89	92	8	7	3	35	43
5	4	7	198	199	9	4	5	34	36	8	5	1	30	24	8	7	4	42	41
5	4	8	94	94	10	4	2	37	17	8	5	4	47	49	8	7	8	47	39
5	4	9	84	84	10	4	8	36	11	8	5	11	44	29	10	7	3	37	7
5	4	10	74	72	11	4	1	42	40	8	5	12	49	34	9	8	0	48	28
5	4	12	42	28	5	5	1	58	59	6	6	0	122	128	10	8	1	41	14
6	4	0	125	122	5	5	2	78	77	6	6	1	55	55	10	8	2	39	18
6	4	1	61	63	5	5	4	23	24	6	6	2	52	56	11	8	5	42	6
6	4	2	81	78	5	5	5	35	40	6	6	3	96	96	9	9	1	54	51
6	4	3	69	71	5	5	6	123	125	6	6	4	70	64	9	9	4	45	24
6	4	4	60	63	5	5	7	63	59	6	6	5	97	94					

Table 2. Positional parameters for the atoms. E.s.d's in parentheses. The corrections of the parameters for rigid-body libration are also listed.

	x	y	z
O2	−.05917 (19)	.34962 (21)	.22186 (11)
	−105	94	6
N1	.15123 (25)	.23443 (24)	.29738 (15)
	35	52	64
C2	.04015 (28)	.24486 (29)	.21805 (16)
	−62	51	−2
N3	.04465 (24)	.14012 (26)	.13617 (15)
	62	−36	−63
C4	.15697 (36)	.03622 (34)	.13582 (23)
	20	−95	−59
C5	.27314 (37)	.02523 (38)	.21401 (21)
	102	−85	5
C6	.26601 (31)	.12748 (34)	.29621 (21)
	108	−17	53
H1	.1500 (26)	.3055 (36)	.3512 (18)
	3	8	8
H4	.1556 (29)	−.0337 (28)	.0715 (22)
	1	−11	−7
H5	.3629 (37)	.0494 (34)	.2101 (23)
	12	−9	−1
H6	.3379 (30)	.1274 (28)	.3587 (20)
	11	1	7

Table 3. Temperature parameters and estimated standard deviations.

Atom	B_{11} (B)	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
O2	.01419 (32)	.01376 (30)	.00543 (13)	.00706 (57)	−.00196 (37)	−.00052 (37)
N1	.01183 (36)	.01207 (36)	.00383 (14)	−.00202 (67)	−.00232 (39)	−.00252 (42)
C2	.00949 (39)	.01170 (41)	.00341 (15)	−.00414 (69)	−.00053 (46)	.00154 (50)
N3	.01389 (40)	.01529 (38)	.00407 (14)	.00431 (66)	−.00232 (41)	−.00310 (44)
C4	.01848 (57)	.01759 (53)	.00522 (19)	.00633(108)	−.00147 (63)	−.00624 (61)
C5	.01608 (57)	.02026 (62)	.00705 (21)	.01235 (97)	−.00262 (67)	−.00579 (67)
C6	.01159 (46)	.01867 (57)	.00621 (22)	.00420 (91)	−.00471 (55)	−.00065 (63)
H1	2.8 (6)					
H4	4.6 (6)					
H5	6.8 (8)					
H6	4.3 (6)					

Table 4. Bond lengths (Å) and angles (°). (a) This investigation, uncorrected values. (b) Estimated standard deviations. (c) This investigation, libration corrected values. (d) Cytosine (uncorrected values).[1] (e) Pyrimidine (uncorrected values).[4]

	(a)	(b)	(c)	(d)	(e)
N1—C2	1.372	0.003	1.384	1.374	1.313
C2—N3	1.356	0.003	1.367	1.364	1.317
N3—C4	1.311	0.003	1.320	1.337	1.332
C4—C5	1.393	0.004	1.403	1.424	1.387
C5—C6	1.346	0.004	1.355	1.342	1.358
C6—N1	1.345	0.003	1.353	1.357	1.343
C2—O2	1.238	0.003	1.244	1.238	
N1—C2—N3	118.3	0.2	118.3	118.1	128.2
C2—N3—C4	118.2	0.2	118.1	119.9	115.1
N3—C4—C5	124.6	0.3	124.7	122.2	122.5
C4—C5—C6	116.8	0.3	116.9	117.3	116.3
C5—C6—N1	119.0	0.3	119.1	120.1	122.7
C6—N1—C2	123.0	0.3	123.0	122.7	115.2
N1—C2—O2	119.8	0.2	119.8	119.8	
N3—C2—O2	121.9	0.2	121.9	122.2	
N1—H1	0.903	0.024	C2—N1—H1	118.5	1.4
C4—H4	0.998	0.026	C6—N1—H1	118.4	1.4
C5—H5	1.002	0.032	N3—C4—H4	113.7	1.4
C6—H6	0.990	0.026	C5—C4—H4	121.6	1.4
			C4—C5—H5	123.9	1.7
			C6—C5—H5	119.2	1.7
			C5—C6—H6	124.4	1.4
			C5—C6—H6	116.6	1.4
Bond lengths and angles involving hydrogen bonds.					
N1—H1···O2	2.796	0.003	C2—O2···H1	113.1	0.6
H1··· O2	1.894	0.025	C2—O2···N1	113.8	0.2
C6—H6···O2	3.250	0.003	C2—O2···H6	111.3	0.6
H6··· O2	2.289	0.026	C2—O2···C6	113.2	0.2
C2—N1···O2	120.8	0.2	N1···O2···C6	113.2	0.1
C6—N1···O2	116.2	0.2	N1···O2···H6	117.9	0.6
N1—C6···O2	106.6	0.2	H1···O2···C6	114.7	0.6
C5—C6···O2	133.6	0.2	H1···O2···H6	119.3	0.8

difference between "observed" U_{ij} and those calculated from the rigid body model was 0.0020 Å^2, indicating a quite good fit. The r.m.s. translational amplitudes were 0.207, 0.177, and 0.158 Å while the r.m.s. librational amplitudes were 6.8, 6.2, and 4.1 degrees. In Tables 2 and 3 the positional and thermal parameters of the atoms are given, as well as the corrections calculated for rigid-body libration. For the hydrogen atoms an isotropic temperature factor was applied.

The atomic scattering factors of Hanson *et al.*[6] were used for the non-hydrogen atoms, those of Stewart *et al.*[7] for the hydrogen atoms. The programs applied were written, or revised, for CDC 3300 by T. Dahl, F. Gram, P. Groth, B. Klewe and Chr. Rømming.

RESULTS AND DISCUSSION

In Table 4 and Fig. 1 bond lengths and angles are given. For comparison, the corresponding values found for pyrimidine and cytosine are also included

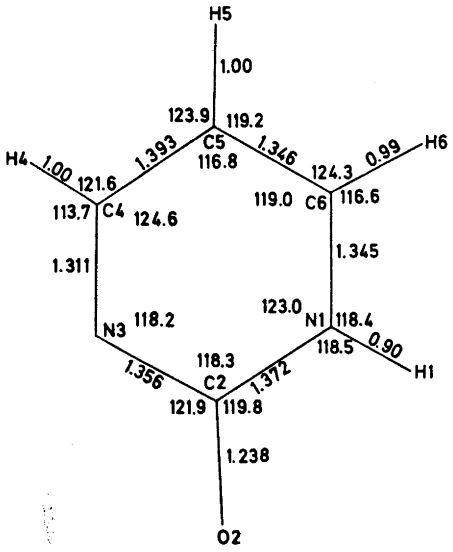

Fig. 1. Bond lengths (Å) and bond angles (uncorrected values).

in Table 4. The compound crystallizes in the oxo form, as to be expected from spectroscopic investigations of its solutions,[8] and as found for all hydroxypyrimidines so far studied in the solid state.

As seen from Table 4 the introduction of a double bonded oxygen atom at C2 significantly changes the bond lengths and angles of the pyrimidine nucleus. The ring angle at C2 is reduced by 10° and the bonds C2–N1 and C2–N3 become longer by about 0.05 Å. The changes in bond lengths corre-

spond in general to a redistribution of bonding electrons in favour of the pairing scheme

It is also of interest to note the changes which occur when an amino group is introduced at C4 in pyrimidine-2-one to give cytosine, the structure of which is well known.[1] Significant changes take place at C4, the bonds C4 – N3

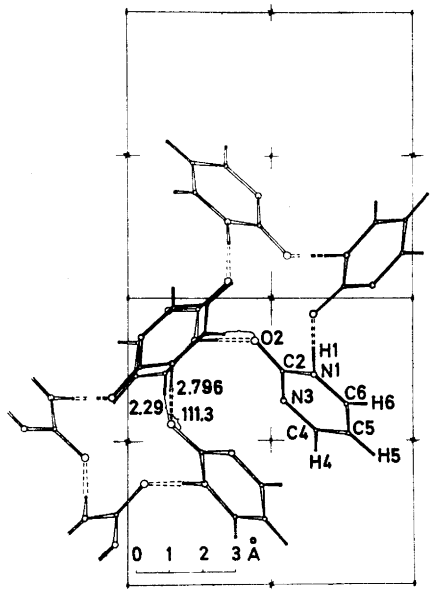

Fig. 2. The *c* projection of the structure.

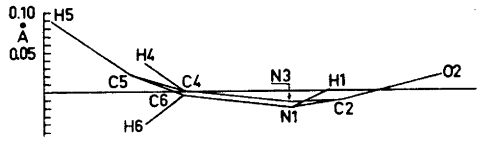

Fig. 3. Deviations from the least squares plane.

and C4 – C5 becoming longer by about 0.02 Å and the ring angle at C4 correspondingly smaller (by 2.4°) when the amino group is introduced. The rest of the molecule is left practically unchanged, apart from small adjustments of the ring angles at N3 and C5.

Deviations from the least squares plane through all non-hydrogen atoms are shown in Fig. 3. Although the molecule is essentially planar, the largest displacements from the plane (0.02 Å) are probably significant. The molecule has a slightly curved, boat-shaped structure, as has been found also in a number of crystal structures of other pyrimidines, for instance cytosine monohydrate.[9] The least squares plane forms an angle of 58.7° with (001) and the distance between neighbouring planes is 3.42 Å.

The arrangement of the molecules in the crystal is shown in Fig. 2. They are linked together by hydrogen bonds N1–H1···O2 of length 2.796 Å in spirals up the four-fold screw axes. The bond is nearly linear and forms an angle of 114° with C2–O2. Neighbouring atoms O2 and N1, to which the molecule is linked by hydrogen bonds, lie close to the molecular plane (to within 0.05 Å). The distance between O2 and H6 in a neighbouring molecule is also also rather short, 2.29 Å; between O2 and C6 3.25 Å. This contact C6–H6···O2 has the stereochemistry of a hydrogen bond, the arrangement being nearly linear, and the angles C2–O2···H6 and H1···O2···H6 having the values of 111.3° and 119.3°, respectively.

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Received March 17, 1970.