The Crystal and Molecular Structure of Epi-inositol

By G. A. Jeffrey and H. S. Kim

Department of Crystallography, University of Pittsburgh, Pittsburgh, Pa. 15213, U.S.A.

The crystal structure of epi-inositol, $C_6H_{12}O_6$, has been determined from Cu $K\alpha$ data obtained with a FACS I automatic diffractometer. The space group is $P2_1/c$, with 4 molecules in the cell with $a=4\cdot841$ (3), $b=14\cdot727$ (4), $c=11\cdot236$ (4) Å, $\beta=115\cdot85°$, $D_m=1\cdot662$, $D_x=1\cdot660$ g.cm^{-3}. The phases were determined by the direct method and the parameters were refined anisotropically by full-matrix least squares to a final $R=0\cdot031$ for 925 observed reflections. The bond lengths are normal with mean C–C and C–O values of $1\cdot527$ and $1\cdot429$ Å. Within experimental error, the molecule has m symmetry. The two axially oriented OH groups give rise to strain in the molecule which causes some flattening of the cyclohexane ring. The molecules are linked by a system of hydrogen bonds such that two OH groups are involved as donor and double acceptor, two as donor and acceptor and two as donor only. The O–(H)$\cdots$O distances vary from $2\cdot731$ to $2\cdot923$ Å. There is some evidence of variation of C–O distances with hydrogen-bond environment; the greater distances corresponding to greatest involvement in the hydrogen bonding.

Introduction

Of the nine stereoisomers of inositol, 1,2,3,4,5,6-cyclo-hexanehexol, $C_6H_{12}O_6$, only myo-inositol, which is the biologically active isomer, has been studied previously by crystal structure determinations. These are of the anhydrous compound by Rabinowitz & Kraut (1964) and of the dihydrate by Lomer, Miller & Beevers (1963). Whereas myo-inositol, (I), has one axially oriented hydroxyl group, epi-inositol, (II), has two. This study was directed principally at an investigation of the effect on the molecular conformation of the axial hydroxyls attached to alternate carbon atoms around the cyclohexane ring. It complements a similar conformational study of the structure of the acyclic hexitols in the crystalline state (Jeffrey & Kim, 1970).

myo
(I)

epi
(II)
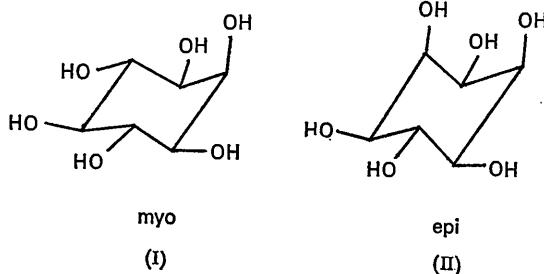
Experimental

Needle-shaped transparent crystals elongated about **a** were obtained by slow evaporation from a solution of ethanol–water at room temperature. The crystals were multiple and frequently occurred in pairs which could be easily recognized both optically and by doubled reflections on X-ray films. Attempts to obtain single crystals from other solvents and at other than room temperatures were unsuccessful. The crystal and intensity data were measured on a FACS I automatic dif-

fractometer with Ni-filtered Cu $K\alpha$ radiation using a crystal pair of dimensions $0\cdot45\times0\cdot05\times0\cdot11$ mm, such that the separate reflections could be resolved without corrections. The crystal density was measured by flotation in a mixture of n-hexane and bromoform at 19°C. The crystal data are as follows:

Monoclinic,
$a=4\cdot841$ (3), $b=14\cdot727$ (4), $c=11\cdot236$ (4) Å,
$\beta=115\cdot85°$;
$V=720\cdot9$ Å^3, $D_m=1\cdot662$, $D_x=1\cdot660$ g.cm^{-3};
$Z=4$, $\mu_{Cu\,K\alpha}=13\cdot26$ cm^{-1}, $(\lambda_{Cu\,K\alpha}=1\cdot5418$ Å).

Space group $P2_1/c$, from the absences of $0k0$ with k odd, $h0l$ with l odd. The intensities were measured with a
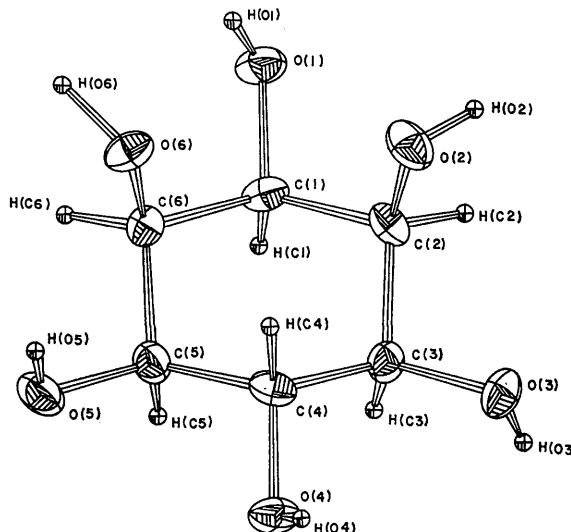

Fig. 1. *ORTEP* plot of epi-inositol, showing atomic notation and thermal ellipsoids. The molecule is viewed approximately normal to the central plane of the chair-shaped cyclohexane ring: C(1) and C(4) are below and above the plane, respectively.

Table 1. *Fractional atomic coordinates and anisotropic thermal parameters in epi-inositol*

The estimated standard deviations are given in parentheses and refer to the last decimal positions. The temperature factor expression used was exp $[-(h^2\beta_{11}+k^2\beta_{22}+l^2\beta_{33}+2hk\beta_{12}+2hl\beta_{13}+2kl\beta_{23})]$.

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
C(1)	0.1075(4)	0.3706(1)	0.3896(2)	0.0174(9)	0.0018(1)	0.0027(2)	0.0001(2)	0.0025(3)	0.0001(1)
C(2)	0.1343(4)	0.4609(1)	0.3280(2)	0.0196(10)	0.0016(1)	0.0035(2)	-0.0006(2)	0.0040(3)	-0.0003(1)
C(3)	-0.1102(4)	0.4636(1)	0.1846(2)	0.0193(10)	0.0015(1)	0.0040(2)	-0.0000(2)	0.0044(3)	0.0005(1)
C(4)	-0.0753(4)	0.3833(1)	0.1068(2)	0.0157(9)	0.0021(1)	0.0028(2)	0.0004(2)	0.0018(3)	0.0000(1)
C(5)	-0.1218(4)	0.2950(1)	0.1670(2)	0.0167(10)	0.0019(1)	0.0035(2)	-0.0004(2)	0.0034(3)	-0.0003(1)
C(6)	0.1139(4)	0.2864(1)	0.3113(2)	0.0215(10)	0.0014(1)	0.0035(2)	0.0002(2)	0.0040(3)	0.0002(1)
O(1)	0.3330(3)	0.3641(1)	0.5248(1)	0.0204(7)	0.0025(1)	0.0026(1)	0.0014(2)	0.0018(2)	-0.0000(1)
O(2)	0.4328(3)	0.4724(1)	0.3335(1)	0.0204(8)	0.0021(1)	0.0060(1)	-0.0016(2)	0.0056(3)	-0.0008(1)
O(3)	-0.0907(3)	0.5476(1)	0.1249(1)	0.0272(8)	0.0018(1)	0.0056(1)	0.0019(2)	0.0057(3)	0.0014(1)
O(4)	-0.3023(3)	0.3871(1)	-0.0287(1)	0.0207(7)	0.0026(1)	0.0025(1)	-0.0011(2)	0.0018(2)	0.0005(1)
O(5)	-0.1123(3)	0.2179(1)	0.0930(1)	0.0191(7)	0.0020(1)	0.0048(1)	-0.0004(2)	0.0031(2)	-0.0010(1)
O(6)	0.4047(3)	0.2723(1)	0.3107(1)	0.0189(7)	0.0021(1)	0.0035(1)	0.0021(2)	0.0029(2)	0.0005(1)

Table 1 (*cont.*)

	x	y	z
H(C1)	-0.088(5)	0.370(1)	0.392(2)
H(C2)	0.092(5)	0.512(1)	0.381(2)
H(C3)	-0.306(5)	0.457(1)	0.182(2)
H(C4)	0.138(5)	0.386(1)	0.108(2)
H(C5)	-0.319(5)	0.302(1)	0.160(2)
H(C6)	0.067(5)	0.232(1)	0.355(2)
H(O1)	0.476(6)	0.344(2)	0.526(2)
H(O2)	0.501(5)	0.521(2)	0.372(2)
H(O3)	-0.235(6)	0.566(2)	0.095(2)
H(O4)	-0.241(6)	0.410(2)	-0.066(2)
H(O5)	0.040(6)	0.210(2)	0.103(2)
H(O6)	0.502(5)	0.232(2)	0.367(2)

$\theta/2\theta$ scan at the rate of 2°/min with stationary background counts. The scan width was varied with 2θ from 2° at $2\theta=10°$ to 4° at the maximum value of $2\theta=130°$. Of the 1234 reflections recorded, 309 had
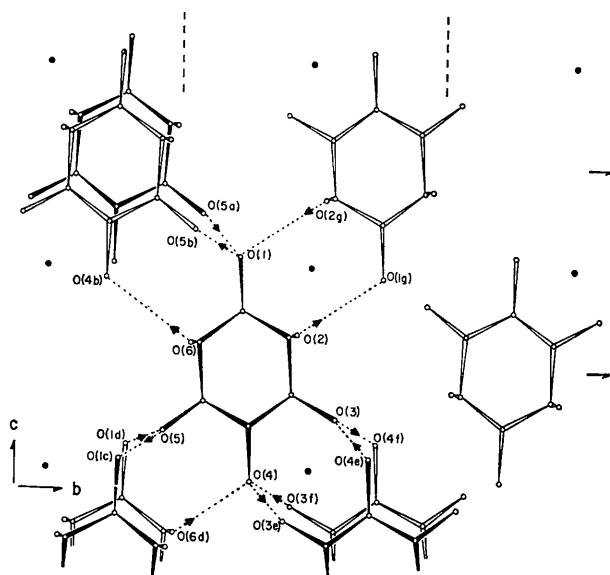

Fig. 2. The crystal structure of epi-inositol viewed down the *a* axis. The dotted lines represent hydrogen bonds, with arrows denoting the donor direction.

intensities above background of less than two standard deviations as estimated from counting statistics; these were recorded as unobserved. No absorption corrections were included in the data reduction.

Structure determination and refinement

The 170 phases of the largest normalized structure amplitudes were generated using direct methods (Long, 1968) on an IBM Model 360/50 computer. The twelve distinctive peaks on the *E* map, calculated from one of the sixteen sets of phases, were consistent with a predicted model of the epi-inositol molecule. Structure factor calculations with a uniform isotropic temperature factor gave an initial *R* index of 0·36 for all reflections. The structure was refined isotropically and anisotropically to an index 0·06 using an IBM 1130 program for block-diagonal least-squares and the same weighting scheme as was used in the final refinement, (Shiono, 1968). All hydrogen atoms were located on a difference synthesis calculated with structure factors within sin $\theta=0·65$ at the *R* index of 0·09. Final refinement with full-matrix least squares on the IBM 7090 computer (Shiono, 1966) included all parameters except the thermal parameters of the hydrogen atoms which were assumed to be the same as the carbon or oxygen atoms to which they are attached. The final parameters are given in Table 1 and the observed structure factors *versus* structure factors calculated from those parameters are listed in Table 2. The final *R* index was 0·031 for observed and 0·049 for all measured reflections.

The weighting scheme, $w^{-1}=(a+b|F_o|+c|F_o|^2)$ with $a=12·06$, $b=1·0$, $c=0·0083$ was used for the final refinement. The thermal parameters are also illustrated by an *ORTEP* plot (Johnson, 1965) in Fig. 1, along with identification of the atoms. The bond lengths and bond angles are given in Table 3.

Discussion

The molecule of epi-inositol, like that of myo-inositol, has the chair conformation with the minimum number

of axially oriented hydroxyl groups, in this case, two, O(2)H and O(6)H, see Fig. 1. The mirror symmetry perpendicular to the cyclohexane plane and passing through C(1) O(1) C(4) O(4), which is ideal for an isolated molecule, is closely maintained in the crystal structure. For the carbon and oxygen atoms, the devia-

Table 2. *Observed and calculated structure factors for epi-inositol*

The columns are: Index, $10|F_{\text{obs}}|$, $10|F_{\text{calc}}|$.* indicates unobserved reflections.

H= 0 K= 0		
2	69	65
4	652	650
6	471	461
8	99	106
10	180	187
H= 0 K= 1		
1	31	33
2	64	65
3	123	121
4	410	411
5	157	162
6	149	142
7	14*	21
8	48	38
9	92	96
10	15*	1
11	63	62
H= 0 K= 2		
0	9*	11
1	502	520
2	28	30
3	254	242
4	140	141
5	511	490
6	134	133
7	126	118
8	109	110
9	253	261
10	112	110
11	77	77
H= 0 K= 3		
1	255	249
2	360	356
3	118	121
4	320	319
5	74	71
6	238	238
7	102	108
8	70	70
9	169	173
10	45	39
11	37	33
H= 0 K= 4		
0	286	289
1	58	55
2	928	925
3	48	45
4	352	360
5	59	59
6	204	208
7	15*	2
8	310	310
9	49	51
10	15*	15
11	47	47
H= 0 K= 5		
1	442	446
2	404	400
3	160	154
4	267	266
5	16*	25
6	35	35
7	97	97
8	158	161
9	15*	12
10	17*	19
11	81	82
H= 0 K= 6		
0	168	165
1	380	375
2	12*	6
3	540	525
4	38	39
5	32	34
6	70	70
7	801	811
8	15*	21
9	15*	3
10	52	52
11	77	71
H= 0 K= 7		
1	118	122
2	152	146
3	86	90
4	14*	0
5	46	10
6	227	226
7	224	226
8	32	24
9	15*	4
10	13*	21
H= 0 K= 8		
0	277	281
1	34	37
2	303	291
3	104	108
4	143	136
5	15*	6
6	57	54
7	16*	4
8	60	63
9	17*	16
10	89	89
H= 0 K= 9		
1	110	105
2	264	266
3	281	286
4	160	154
5	48	40
6	164	168
7	98	97
8	16*	3
9	51	49
10	69	66
H= 0 K= 10		
0	67	68
1	359	365
2	41	40
3	166	159
4	45	41
5	292	302
6	60	57
7	99	102
8	37	35
9	173	172
H= 0 K= 11		
1	199	205
2	51	48
3	14*	22
4	38	36
5	114	116
6	128	132
7	45	41
8	110	107
9	31	25
H= 0 K= 12		
0	645	662
1	85	85
2	34	32
3	115	116
4	201	208
5	62	65
6	131	139
7	38	38
8	36	28
H= 0 K= 13		
1	189	188
2	15*	9
3	37	35
4	62	69
5	33	26
6	60	61
7	48	45
H= 0 K= 14		
0	22*	22
1	16*	21
2	34	31
3	61	61
4	15*	28
5	14*	22
6	58	57
H= 0 K= 15		
1	53	51
2	62	56
3	140	134
4	126	128
5	59	55
H= 0 K= 16		
0	143	144
1	14*	15
2	145	139
3	35	35
4	32	29
H= 0 K= 17		
1	93	90
2	31	32
H= 1 K= 0		
0	627	640
2	694	702
4	1056	1048
6	407	407
8	67	78
10	97	91
H= 1 K= 1		
0	68	67
1	240	248
2	110	113
3	278	273
4	12*	13
5	31	23
6	110	112
7	15*	9
8	75	70
9	14*	4
10	39	39
H= 1 K= 2		
0	11*	21
1	418	409
2	97	94
3	66	58
4	13*	12
5	202	195
6	15*	26
7	34	25
8	72	73
9	53	45
10	49	54
H= 1 K= 3		
0	69	73
1	226	233
2	211	219
3	165	166
4	240	238
5	69	73
6	14*	3
7	88	92
8	113	110
9	43	34
10	35	32
H= 1 K= 4		
0	36	27
1	74	69
2	625	605
3	75	74
4	119	111
5	127	127
6	306	304
7	16*	21
8	144	145
9	71	73
10	53	46
H= 1 K= 5		
0	102	108
1	137	132
2	68	60
3	115	113
4	169	172
5	225	225
6	195	199
7	96	96
8	16*	24
9	14*	9
10	72	71
H= 1 K= 6		
0	90	96
1	52	54
2	104	106
3	37	42
4	69	69
5	261	265
6	16*	15
7	223	224
8	15*	1
9	132	130
H= 1 K= 7		
0	176	177
1	131	141
2	63	54
3	138	136
4	125	123
5	85	85
6	50	51
7	16*	10
8	94	95
9	36	34
H= 1 K= 8		
0	209	202
1	14*	26
2	45	47
3	14*	0
4	104	101
5	126	125
6	281	273
7	16*	14
8	90	89
9	64	62
H= 1 K= 9		
0	271	274
1	285	291
2	15*	27
3	119	122
4	173	184
5	60	60
6	145	146
7	49	48
8	32	32
H= 1 K= 10		
0	15*	24
1	222	215
2	15*	34
3	128	136
4	39	40
5	161	171
6	15*	3
7	38	44
8	42	45
H= 1 K= 11		
0	121	124
1	15*	13
2	79	80
3	16*	24
4	33	31
5	146	149
6	31	34
7	65	57
H= 1 K= 12		
0	275	280
1	15*	15
2	148	153
3	58	58
4	318	322
5	39	37
6	90	91
7	36	37
H= 1 K= 13		
0	78	81
1	133	136
2	15*	27
3	79	77
4	90	90
5	133	136
6	13*	25
H= 1 K= 14		
0	15*	19
1	50	49
2	14*	2
3	15*	14
4	14*	18
5	13*	7
H= 1 K= 15		
0	34	31
1	14*	16
2	94	93
3	103	107
4	56	58
H= 1 K= 16		
0	14*	9
1	31	28
2	85	85
3	12*	14
H= 2 K= 0		
0	229	220
2	334	338
4	137	132
6	70	61
8	33	17
H= 2 K= 1		
0	330	326
1	108	106
2	46	39
3	14*	29
4	137	136
5	162	160
6	16*	26
7	16*	16
8	34	40
9	45	46
H= 2 K= 2		
0	36	27
1	299	289
2	14*	23
3	380	366
4	157	156
5	169	165
6	48	51
7	106	114
8	39	38
9	46	41
H= 2 K= 3		
0	330	331
1	163	163
2	39	32
3	146	151
4	114	117
5	15*	2
6	50	50
7	53	57
8	14*	12
H= 2 K= 4		
0	347	335
1	13*	13
2	37	23
3	15*	27
4	15*	0
5	15*	3
6	56	60
7	91	90
8	85	84
H= 2 K= 5		
0	61	42
1	66	58
2	33	15
3	35	30
4	97	93
5	83	83
6	46	44
7	95	96
8	73	75
H= 2 K= 6		
0	14*	15
1	53	26
2	14*	10
3	308	307
4	36	40
5	436	435
6	65	64
7	14*	13
8	13*	1
H= 2 K= 7		
0	52	43
1	14*	13
2	110	111
3	34	31
4	103	100
5	64	68
6	51	48
7	84	86
8	13*	9
H= 2 K= 8		
0	61	51
1	15*	25
2	130	129
3	15*	6
4	139	130
5	32	29
6	46	49
7	82	82
H= 2 K= 9		
0	76	71
1	113	112
2	71	67
3	92	90
4	121	123
5	51	52
6	74	77
7	99	100
H= 2 K= 10		
0	45	39
1	204	200
2	16*	19
3	126	127
4	15*	2
5	31	27
6	14*	12
H= 2 K= 11		
0	98	99
1	70	67
2	68	67
3	39	37
4	175	178
5	75	77
6	12*	3
H= 2 K= 12		
0	60	62
1	41	41
2	246	243
3	85	85
4	139	143
5	13*	17
H= 2 K= 13		
0	15*	11
1	44	38
2	106	115
3	45	42
4	74	76
H= 2 K= 14		
0	15*	11
1	78	77
2	15*	26
3	171	170
H= 2 K= 15		
0	136	138
1	43	49
2	58	56
H= 3 K= 0		
0	92	99
2	805	820
4	48	46
6	15*	10
H= 3 K= 1		
0	125	124
1	16*	35
2	105	104
3	16*	7
4	56	54
5	16*	27
6	96	94
7	13*	24
H= 3 K= 2		
0	36	29
1	153	148
2	60	61
3	117	114
4	16*	12
5	45	45
6	106	110
H= 3 K= 3		
0	118	114
1	59	60
2	225	223
3	16*	15
4	92	91
5	77	79
6	66	59
H= 3 K= 4		
0	287	297
1	15*	20
2	16*	29
3	43	43
4	273	276
5	35	36
6	14*	11
H= 3 K= 5		
0	163	160
1	170	171
2	120	121
3	75	73
4	121	123
5	14*	20
6	61	59
H= 3 K= 6		
0	17*	31
1	50	49
2	15*	21
3	253	250
4	15*	10
5	177	181
6	39	39
H= 3 K= 7		
0	52	48
1	15*	15
2	38	36
3	70	71
4	123	127
5	14*	24
H= 3 K= 8		
0	167	164
1	92	92
2	95	93
3	55	54
4	125	126
5	36	37
H= 3 K= 9		
0	153	155
1	58	60
2	61	60
3	46	43
4	68	65
H= 3 K= 10		
0	15*	1
1	146	145
2	15*	14
3	198	205
4	14*	18
H= 3 K= 11		
0	15*	11
1	86	88
2	15*	3
3	79	77
H= 3 K= 12		
0	105	105
1	71	72
2	353	357
H= 3 K= 13		
0	14*	12
1	139	139
H= 3 K= 14		
0	13*	3
H= 4 K= 0		
0	466	462
2	127	128
4	165	160
H= 4 K= 1		
0	91	88
1	167	173
2	16*	10
3	53	49
4	57	61
H= 4 K= 2		
0	79	80
1	250	247
2	15*	10
3	97	98
4	13*	1
H= 4 K= 3		
0	16*	25
1	32	27
2	39	36
3	14*	6
4	41	42
H= 4 K= 4		
0	138	140
1	47	45
2	48	47
3	66	66
4	88	88
H= 4 K= 5		
0	90	88
1	45	46
2	60	54
3	68	68
H= 4 K= 6		
0	16*	22
1	107	110
2	46	46
3	116	119
H= 4 K= 7		
0	40	36
1	14*	10
2	80	82
H= 4 K= 8		
0	14*	11
1	50	46
2	55	52
H= 4 K= 9		
0	15*	21
1	87	86
H= 4 K= 10		
0	14*	24
1	168	172
H= 5 K= 0		
0	281	287
H= 5 K= 1		
0	14*	11
H= 5 K= 2		
0	13*	10
H= 5 K= 3		
0	64	63
H= 5 K= 4		
0	76	78
H= -1 K= 0		
2	1041	1127
4	12*	10
6	12*	3
8	325	317
10	421	425
12	50	48
H= -1 K= 1		
1	353	360
2	491	501
3	356	360
4	158	167
5	78	80
6	138	132
7	215	218
8	51	43
9	32	29
10	157	161
11	16*	28
12	83	85
H= -1 K= 2		
1	810	864
2	81	82
3	301	297
4	116	121
5	466	454
6	155	158
7	167	163
8	60	60
9	16*	9
10	15*	0
11	144	147
12	52	56
H= -1 K= 3		
1	109	108
2	388	398
3	374	381
4	263	261
5	204	206
6	176	178
7	124	126
8	69	75
9	124	125
10	32	27
11	62	66
12	74	77
H= -1 K= 4		
1	57	60
2	271	274
3	54	54
4	332	328
5	128	131
6	307	299
7	69	68
8	261	263
9	148	153
10	35	44
11	56	54
12	99	104
H= -1 K= 5		
1	98	96
2	361	374
3	181	187
4	56	55
5	179	178
6	79	78
7	15*	28
8	65	61
9	246	249
10	39	40
11	15*	6
12	72	73
H= -1 K= 6		
1	633	626
2	35	35
3	1056	1061
4	80	81
5	349	329
6	15*	25
7	169	169
8	91	96
9	332	332
10	16*	21
11	37	35
H= -1 K= 7		
1	43	39
2	249	256
3	132	130
4	89	89
5	155	152
6	49	50
7	128	133
8	16*	16
9	86	88
10	15*	28
11	14*	23
H= -1 K= 8		
1	14*	27
2	168	159
3	13*	1
4	45	38
5	64	64
6	90	82
7	15*	6
8	264	265
9	116	119
10	115	110
11	62	59
H= -1 K= 9		
1	61	62
2	89	89
3	89	89
4	120	123
5	183	178
6	15*	4
7	16*	32
8	36	34
9	87	84
10	80	78
H= -1 K= 10		
1	199	213
2	54	58
3	65	62
4	15*	18
5	280	257
6	16*	19
7	16*	36
8	16*	19
9	14*	3
10	48	48
H= -1 K= 11		
1	137	136
2	280	286
3	91	88
4	16*	2
5	56	53
6	40	42
7	53	48
8	65	70
9	126	126
H= -1 K= 12		
1	138	141
2	316	319
3	16*	19
4	46	44
5	60	59
6	63	77
7	14*	6
8	48	46
9	65	64
H= -1 K= 13		
1	16*	4
2	131	132
3	70	70
4	15*	4
5	45	44
6	48	48
7	68	72
8	81	77
H= -1 K= 14		
1	205	202
2	15*	1
3	86	80
4	65	63
5	39	44
6	14*	23
7	73	79
H= -1 K= 15		
1	78	77
2	77	78
3	108	112
4	117	114
5	14*	2
6	116	117
H= -1 K= 16		
1	55	56
2	91	85
3	14*	5
4	124	119
5	45	47
H= -1 K= 17		
1	12*	5
H= -2 K= 0		
2	1107	1168
4	696	698
6	88	79
8	45	39
10	45	42
12	206	206
H= -2 K= 1		
1	310	328
2	13*	24
3	12*	11
4	154	160
5	74	80
6	35	19
7	47	40
8	132	134
9	62	70
10	88	85
11	15*	12
12	98	94
13	13*	6
H= -2 K= 2		
1	97	88
2	32	36
3	222	205
4	66	69
5	30	20
6	41	39
7	57	57
8	41	37
9	62	61
10	111	110
11	204	204
12	33	30
13	61	65
H= -2 K= 3		
1	185	178
2	31	30
3	145	145
4	238	250
5	13*	9
6	165	166
7	14*	7
8	15*	6
9	16*	26
10	16*	15
11	120	116
12	42	43
H= -2 K= 4		
1	12*	9
2	162	152
3	129	143
4	238	232
5	49	53
6	330	327
7	130	128
8	71	63
9	15*	1
10	137	139
11	72	70
12	91	91
H= -2 K= 5		
1	104	93
2	298	299
3	357	363
4	92	85
5	189	188
6	14*	7
7	144	143
8	204	206
9	16*	25
10	73	75
11	15*	4
12	53	49
H= -2 K= 6		
1	87	84
2	72	76
3	65	57
4	100	103
5	429	422
6	64	67
7	100	107
8	16*	14
9	366	377
10	16*	19
11	94	93
12	13*	18
H= -2 K= 7		
1	91	90
2	127	125
3	14*	30
4	51	55
5	15*	14
6	94	92
7	48	40
8	116	118
9	154	148
10	96	95
11	84	86
12	12*	3
H= -2 K= 8		
1	14*	23
2	63	63
3	14*	7
4	420	413
5	33	36
6	85	81
7	121	122
8	15*	5
9	16*	0
10	104	106
11	35	33
H= -2 K= 9		
1	81	80
2	97	95
3	136	133
4	179	177
5	83	83
6	125	120
7	189	182
8	134	141
9	15*	10
10	14*	10
11	39	33
H= -2 K= 10		
1	34	11
2	15*	6
3	74	78
4	15*	15
5	44	48
6	75	78
7	95	112
8	15*	13
9	49	42
10	77	73
H= -2 K= 11		
1	16*	1
2	16*	26
3	137	141
4	43	45
5	104	100
6	16*	23
7	40	38
8	15*	3
9	38	40
10	59	61
H= -2 K= 12		
1	117	120
2	390	396
3	16*	10
4	61	57
5	16*	28
6	39	16
7	32	30
8	14*	2
9	47	49
H= -2 K= 13		
1	75	78
2	92	89
3	175	170
4	58	56
5	52	49
6	36	36
7	14*	4
8	14*	11
H= -2 K= 14		
1	15*	28
2	15*	9
3	113	113
4	15*	1
5	70	66
6	14*	3
7	66	56
H= -2 K= 15		
1	118	124
2	14*	5
3	40	33
4	63	58
5	62	57
6	39	38
H= -2 K= 16		
1	28	33
2	33	29
3	60	57
H= -3 K= 0		
2	531	509
4	691	671
6	19*	20
8	73	75
10	56	53
12	374	375
H= -3 K= 1		
1	84	80
2	106	95
3	188	183
4	109	105
5	76	80
6	199	198
7	106	106
8	105	102
9	112	114
10	16*	26
11	87	89
12	119	115
13	36	37
H= -3 K= 2		
1	78	78
2	42	38
3	359	344
4	37	37
5	36	35
6	33	31
7	263	260
8	112	112
9	150	145
10	45	44
11	33	31
12	51	54
13	160	160
H= -3 K= 3		
1	14*	14
2	36	38
3	38	40
4	110	109
5	73	89
6	15*	24
7	212	214
8	170	167
9	16*	16
10	59	58
11	119	118
12	14*	18
H= -3 K= 4		
1	59	58
2	361	347
3	15*	18
4	238	248
5	35	33
6	267	272
7	70	69
8	17*	31
9	16*	10
10	222	224
11	78	77
12	36	33
H= -3 K= 5		
1	168	165
2	129	133
3	49	50
4	15*	24
5	15*	17
6	194	195
7	42	41
8	52	51
9	77	75
10	42	38
11	97	97
12	48	47
H= -3 K= 6		
1	82	89
2	85	87
3	15*	18
4	31	29
5	731	753
6	16*	12
7	101	98
8	17*	27
9	187	187
10	16*	21
11	262	271
12	38	37
H= -3 K= 7		
1	119	119
2	75	76
3	64	65
4	161	164
5	134	136
6	84	81
7	16*	25
8	16*	19
9	122	125
10	15*	23
11	75	79
H= -3 K= 8		
1	16*	17
2	16*	27
3	16*	4
4	16*	16
5	16*	3
6	111	108
7	15*	6
8	37	37
9	15*	10
10	54	61
11	44	42
H= -3 K= 9		
1	222	222
2	122	121
3	56	57
4	142	144
5	119	119
6	73	72
7	42	43
8	63	60
9	56	61
10	52	56
11	50	49
H= -3 K= 10		
1	15*	12
2	16*	27
3	270	281
4	61	61
5	144	146
6	53	47
7	149	143
8	16*	26
9	112	119
10	14*	12
H= -3 K= 11		
1	65	61
2	16*	2
3	99	102
4	121	123
5	64	65
6	114	111
7	15*	28
8	14*	5
9	119	123
H= -3 K= 12		
1	15*	7
2	160	165
3	62	62
4	201	212
5	62	64
6	15*	3
7	14*	14
8	88	69
H= -3 K= 13		
1	64	62
2	35	35
3	46	45
4	15*	22
5	39	39
6	60	57
7	14*	21
H= -3 K= 14		
1	44	49
2	14*	7
3	13*	2
4	13*	11
5	94	93
6	39	36
H= -4 K= 0		
2	100	101
4	193	168
6	121	124
8	378	378
10	178	176
12	40	34
H= -4 K= 1		
1	107	107
2	56	52
3	16*	3
4	183	177
5	192	190
6	53	50
7	44	46
8	101	101
9	17*	8
10	34	36
11	44	45
12	53	58
H= -4 K= 2		
1	16*	29
2	16*	6
3	149	151
4	16*	7
5	144	130
6	41	34
7	37	39
8	16*	14
9	150	145
10	16*	5
11	15*	7
12	13*	1
H= -4 K= 3		
1	184	181
2	93	91
3	15*	5
4	98	99
5	118	120
6	155	156
7	16*	7
8	47	50
9	106	105
10	15*	20
11	14*	14
12	34	34
H= -4 K= 4		
1	16*	1
2	178	181
3	35	28
4	121	120
5	50	48
6	233	238
7	63	64
8	80	80
9	58	61
10	146	150
11	51	53
12	80	83
H= -4 K= 5		
1	49	52
2	16*	5
3	17*	15
4	17*	35
5	16*	16
6	176	175
7	241	240
8	16*	14
9	15*	7
10	38	33
11	84	85
H= -4 K= 6		
1	339	344
2	16*	18
3	242	244
4	16*	11
5	109	109
6	65	66
7	447	448
8	16*	12
9	37	36
10	32	30
11	78	84
H= -4 K= 7		
1	16*	24
2	65	66
3	16*	16
4	66	67
5	63	65
6	38	43
7	103	106
8	49	48
9	15*	17
10	14*	2
11	95	93
H= -4 K= 8		
1	16*	24
2	15*	20
3	16*	6
4	15*	11
5	16*	3
6	184	180
7	16*	22
8	85	86
9	65	59
10	14*	17
H= -4 K= 9		
1	108	112
2	14*	0
3	15*	13
4	73	73
5	15*	19
6	37	36
7	16*	24
8	104	96
9	131	129
H= -4 K= 10		
1	74	75
2	14*	9
3	162	164
4	15*	8
5	74	77
6	15*	6
7	101	99
8	40	31
9	157	150
H= -4 K= 11		
1	13*	3
2	15*	19
3	45	45
4	56	54
5	61	64
6	57	54
7	114	116
8	13*	16
H= -4 K= 12		
2	13*	4
3	58	58
4	114	115
5	14*	28
6	14*	17
H= -5 K= 0		
2	75	80
4	64	55
6	15*	6
8	108	105
10	191	195
H= -5 K= 1		
1	61	61
2	15*	28
3	17*	34
4	70	73
5	16*	37
6	16*	24
7	57	57
8	58	53
9	55	55
10	117	120
H= -5 K= 2		
1	84	79
2	16*	25
3	15*	3
4	15*	4
5	15*	14
6	15*	9
7	40	38
8	15*	8
9	136	138
10	14*	10
H= -5 K= 3		
1	32	33
2	128	130
3	64	62
4	15*	13
5	15*	10
6	33	38
7	55	52
8	15*	18
9	103	104
10	63	61
H= -5 K= 4		
1	15*	8
2	113	122
3	15*	1
4	72	74
5	15*	22
6	49	51
7	15*	20
8	64	59
9	62	58
10	47	43
H= -5 K= 5		
1	82	81
2	80	86
3	97	98
4	66	68
5	118	120
6	73	69
7	35	31
8	14*	9
9	55	59
H= -5 K= 6		
1	33	34
2	14*	30
3	202	209
4	14*	17
5	44	45
6	43	46
7	253	255
8	14*	12

Table 3. *Bond lengths and bond angles in epi-inositol*

Estimated standard deviations in parentheses refer to the last decimal positions of respective values.

$\bar{l}(C-C) = 1\cdot527$ (2) Å $\qquad$ $<(\overline{C-C-C}) = 110\cdot8$ (2·1)°
$\bar{l}(C-O) = 1\cdot430$ (7) $\qquad$ $<(\overline{C-C-O}) = 110\cdot5$ (1·9)

The mean values and estimated standard deviations are calculated from

$$\bar{l} = \sum_{i=1}^{N} \left(\frac{l_i}{\sigma_i^2} \right) \Big/ \sum_{i=1}^{N} \left(\frac{1}{\sigma_i^2} \right), \quad \sigma_{mean} = \left[\frac{\sum_{i=1}^{N} (\bar{l}-l_i)^2}{N-1} \right]^{1/2}.$$

| i	j	D(ij)	i	j	k	<(ijk)
C(1)	C(2)	1·530 (3) Å	C(1)	C(2)	C(3)	108·7 (2)°
C(2)	C(3)	1·528 (3)	C(2)	C(3)	C(4)	110·8 (2)
C(3)	C(4)	1·523 (3)	C(3)	C(4)	C(5)	109·4 (2)
C(4)	C(5)	1·526 (3)	C(4)	C(5)	C(6)	110·8 (2)
C(5)	C(6)	1·527 (3)	C(5)	C(6)	C(1)	110·5 (2)
C(6)	C(1)	1·528 (3)	C(6)	C(1)	C(2)	114·7 (2)
C(1)	O(1)	1·435 (2)	C(2)	C(1)	O(1)	111·2 (1)
C(2)	O(2)	1·429 (2)	C(6)	C(1)	O(1)	111·0 (1)
C(3)	O(3)	1·429 (2)	C(1)	C(2)	O(2)	111·6 (2)
C(4)	O(4)	1·439 (2)	C(3)	C(2)	O(2)	110·2 (1)
C(5)	O(5)	1·419 (2)	C(2)	C(3)	O(3)	109·8 (1)
C(6)	O(6)	1·426 (2)	C(4)	C(3)	O(3)	110·9 (2)
			C(3)	C(4)	O(4)	110·6 (1)
C(1)	H(C1)	0·96 (2)	C(5)	C(4)	O(4)	108·1 (1)
C(2)	H(C2)	1·04 (2)	C(4)	C(5)	O(5)	111·9 (2)
C(3)	H(C3)	0·94 (2)	C(6)	C(5)	O(5)	110·8 (2)
C(4)	H(C4)	1·03 (3)	C(1)	C(6)	O(6)	112·9 (2)
C(5)	H(C5)	0·93 (2)	C(5)	C(6)	O(6)	106·8 (1)
C(6)	H(C6)	1·02 (2)				
O(1)	H(O1)	0·74 (3)				
O(2)	H(O2)	0·84 (3)				
O(3)	H(O3)	0·69 (3)				
O(4)	H(O4)	0·70 (3)				
O(5)	H(O5)	0·71 (3)				
O(6)	H(O6)	0·85 (3)				
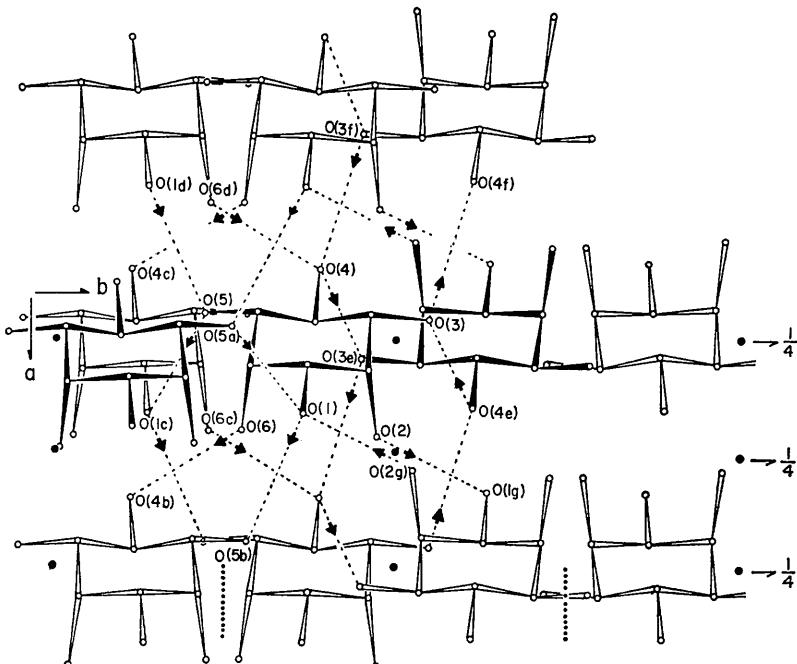
Fig. 3. The crystal structure of epi-inositol viewed down the *c* axis. The dotted lines represent hydrogen bonds, with arrows denoting the donor direction.

Table 4. *Hydrogen bond distances and angles in epi-inositol*

i	j	k	l	m	D(jl)	<(ijl)	<(jkl)	<(jlm)
C(1)	O(1)	H(O1)	O(5b)	C(5b)	2·731 Å	121·9°	160·6°	103·9°
C(2)	O(2)	H(O2)	O(1g)	C(1g)	2·836	105·9	176·8	118·1
C(3)	O(3)	H(O3)	O(4f)	C(4f)	2·820	101·8	169·9	127·3
C(4)	O(4)	H(O4)	O(3e)	C(3e)	2·739	95·2	157·4	133·5
C(5)	O(5)	H(O5)	O(1c)	C(1c)	2·852	135·8	143·9	89·8
C(6)	O(6)	H(O6)	O(4b)	C(4b)	2·923	109·2	167·4	124·2

Table 4 (*cont.*)

Non-bonded O···O distances less than 3·2 Å

i	j	D(ij)
O(1)	O(2)	2·881 Å
O(1)	O(6)	2·909
O(2)	O(3)	2·821
O(2)	O(6)	2·957
O(3)	O(4)	2·841
O(4)	O(5)	2·798
O(5)	O(6)	2·747
O(5)	O(6d)	3·014

Symmetry code

	x	y	z
(a)	x	$\frac{1}{2}-y$	$\frac{1}{2}+z$
(b)	1+x	$\frac{1}{2}-y$	$\frac{1}{2}+z$
(c)	x	$\frac{1}{2}-y$	$-\frac{1}{2}+z$
(d)	−1+x	$\frac{1}{2}-y$	$-\frac{1}{2}+z$
(e)	−x	1−y	−z
(f)	−1−x	1−y	−z
(g)	1−x	1−y	1−z

tions from *m* symmetry are less than 0·01 Å. The methylene hydrogen atoms are also symmetrical within the rather large estimated errors in their positions. The hydroxyl hydrogen atoms depart significantly from this molecular symmetry. This is expected because the orientation of the OH groups is determined by the intermolecular hydrogen bonding rather than by intramolecular forces, and the *m* molecular symmetry is not included in the crystal structure symmetry (see Fig. 2).

The C–C bond lengths range from 1·523 to 1·530 Å with a mean of 1·527 Å. In myo-inositol, the range is 1·508 to 1·533 with a mean of 1·521 Å. These differences are not significant. The C–O bonds vary over a wider range of 1·419 to 1·439 Å. The two longer bonds, C(4)–O(4) 1·439 Å and C(1)–O(1) 1·435 Å are associated with oxygen atoms involved in three hydrogen bonds, whereas the four shorter distances 1·429 to 1·419 Å correspond to oxygen atoms involved in only one or two hydrogen bonds. This is a marginal observation in terms of the estimated errors and requires verification by means of a more precise investigation of a neutron diffraction study which could reveal any related correlation with O–H distances.

The intermolecular hydrogen-bonding is shown in Figs. 2 and 3. It consists of two branched infinite chains shown diagrammatically as follows:

O(3) → O(4) → O(3) → O(4)
↓   ↓
O(6)   O(6)

O(1) → O(5) → O(1) → O(5)
↓   ↓
O(2)   O(2)
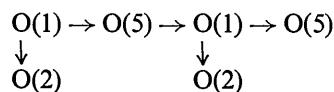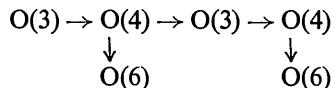
The hydrogen bond distances and angles are given in Table 4. The intermolecular O(H)···O distances range from 2·731 to 2·923 Å and are comparable in magnitude to the intramolecular O···O distances. There is also one intermolecular O···O non-bonding distance less than 3·2 Å as given in Table 4.

The intramolecular O(2)···O(6) distance is 2·96 Å, as compared with 2·50 Å in an unstrained cyclohexane ring with 60° dihedral angles. The effect of this strain interaction as compared with the ideal model is illustrated in Fig. 4.
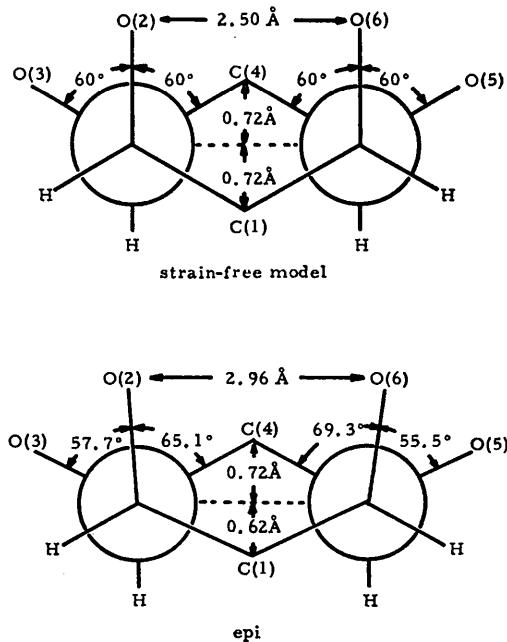
Fig. 4. Conformational angles in the epi-inositol. The conformational views are down C(2)–C(3) and C(6)–C(5). The strain-free model is based on C–C, 1·527 Å and tetrahedral angles. The mean value for the C–C–C ring angle is 109·7° in the two molecules of myo-inositol and 110·0° in epi-inositol [excluding that at C(1)]. There is, therefore, no justification for using the larger C–C–C angle of about 112° commonly observed in acylic hydrocarbons and carbohydrates, cf. Eliel, Allinger, Angyal & Morrison (1967).

References

ELIEL, E. L., ALLINGER, N. L., ANGYAL, S. J. & MORRISON, G. A. (1967). *Conformational Analysis*, p. 455. New York: Interscience.

JEFFREY, G. A. & KIM, H. S. (1970). *Carbohydrate Res.* **14**, 207.

JOHNSON, C. K. (1965). *ORTEP. A Fortran Thermal Ellipsoid Plot Program for Crystal Structure Illustration.* Report No. ORNL-3794, Oak Ridge National Laboratory, Tennessee.

LOMER, T. R., MILLER, A. & BEEVERS, C. A. (1963). *Acta Cryst.* **16**, 264.

LONG, R. E. (1965). *A Program for Phase Determination by Reiterative Application of Sayre's Equation.* Ph. D. Thesis, U.C.L.A.

RABINOWITZ, I. N. & KRAUT, J. (1964). *Acta Cryst.* **17**, 159.

SHIONO, R. (1966). Oak Ridge Least Squares Program, modified for the Department of Crystallography of the Univ. of Pittsburgh.

SHIONO, R. (1968). *IBM* 1130 *Least-Squares Program.* Technical Report, Department of Crystallography, Univ. of Pittsburgh.

The Crystal Structure of 4,4'-Diacetoxy-5,5'-dimethyl-2,2'-bithiazolyl (C12H12N2S2O4)*

BY K. J. PALMER, ROSALIND Y. WONG AND KAY S. LEE

Western Regional Research Laboratory, Agricultural Research Service,
U.S. Department of Agriculture, Albany, California 94710, U.S.A.

The reaction product of α-mercapto acids with cyanogen undergoes unusual N-methylation in addition to esterification when treated with diazomethane and converts to the bicyclic symmetrical 4,4'-diketo-Δ^2-bithiazolinyl. The structure of the bicyclic compound has been a moot question for many years. Some investigations favored two six-membered rings with a shared edge; others, two five-membered rings bonded together. A crystal-structure determination of 4,4'-diacetoxy-5,5'-dimethyl-2,2'-bithiazolyl proves that this compound consists of two five-membered rings joined by a C–C bond. The crystallographic data for the monoclinic crystals are $a = 13 \cdot 125 \pm 0 \cdot 005$, $b = 4 \cdot 830 \pm 0 \cdot 002$, $c = 10 \cdot 995 \pm 0 \cdot 004$ Å, $\beta = 94 \cdot 09 \pm 0 \cdot 01°$, $Z = 2$, space group $P2_1/c$. The intensities of 1367 independent reflections were measured with an automatic diffractometer. Least-squares refinement with anisotropic thermal parameters for the ten heavy atoms and isotropic thermal parameters for the hydrogen atoms gave an R value of 0·050.

In their studies of the reaction of α-mercapto acids with cyanogen, Mutha & Ketchum (1968) found that the reaction between mercaptoacetic acid and cyanogen (Fig. 1) gave a white crystalline product which proved to be monocyclic. Cyclization can result in the formation of a five-membered ring [Fig. 1(*a*)] or a six-membered ring [Fig. 1 (*b*)]. Their study of the ultraviolet (UV), infrared (IR), and nuclear magnetic resonance (n.m.r) spectra of this product and several derivatives did not furnish a clear distinction between the two structures.

To obtain additional information, Mutha & Ketchum synthesized a bicyclic compound whose structure after acetylation, was either that of Fig. 2(*a*) or 2(*b*). Their study of the UV, IR, and n.m.r. spectra and a dipole-moment determination again failed to provide an unequivocal assignment of structure. Attempts to grow crystals suitable for X-ray analysis, from the various derivatives of both the monocyclic and bicyclic

compounds, led to the selection of the diacetate derivative of the bicyclic compound for crystal-structure analysis. The compound turned out to be 4,4'-diacetoxy-5,5'-dimethyl-2,2'-bithiazolyl, hereafter referred to as DDB.

Experimental

The material used in this investigation was provided by Professor R. Ketchum and Dr S. Mutha. Crystals suitable for X-ray analysis were grown from chloroform. The crystals are elongated prisms with **b** parallel to the long axis and (100) prominent. The crystals cleave easily, parallel to the **ab** plane, but cannot be cut perpendicular to **b** without introducing X-ray line broadening. Consequently, the intensity data were taken on an uncut specimen with dimensions of $0 \cdot 07 \times 0 \cdot 20 \times 0 \cdot 14$ mm.

Multiple-level Weissenberg photographs showed that the only systematic absences are $0k0$ when k is odd, and $h0l$ when l is odd. These extinctions indicate space group $P2_1/c$ which was confirmed by the struc-

---
* Presented at the American Crystallographic Association meeting, August 16-22, 1970, Ottawa, Canada.