Acta Cryst. (1971). B27, 1917

The Crystal Structure of Polymorph IV of 5,5-Diethylbarbituric Acid (Barbital)

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(*Received* 30 *November* 1970)

Supposedly, six polymorphs of 5,5-diethylbarbituric acid (barbital) exist. The crystal structures of polymorphs I and II were determined by Craven, Vizzini & Rodrigues (*Acta Cryst.* (1969) B25, 1978). We now report the crystal structure determination of polymorph IV, and also present evidence that suggests polymorphs II and III are identical. Barbital IV (m.p. 176°C) is monoclinic, with $a = 12{\cdot}585$ (8), $b = 22{\cdot}083$ (10), $c = 6{\cdot}788$ (9) Å, $\beta = 90°55$ (2)′ and space group $P2_1$ with eight molecules per cell. X-ray intensity data (2910 reflections) were collected using nickel-filtered Cu $K\alpha$ radiation and a computer-controlled four-circle diffractometer. The phase problem was solved by comparing barbital IV with the closely related crystal structures of vinbarbital and heptabarbital. Least-squares refinement was in five large parameter blocks to give a final R value of 0·05. The 660 structure parameters included positional parameters for all atoms, and thermal parameters that were anisotropic for the heavier atoms and isotropic for hydrogen atoms. Bond distances, angles, and molecular conformations are similar to those in barbital I and II. The crystal structures of polymorphs I, II, and IV differ in the geometry of their NH···O=C hydrogen-bonded frameworks.

Introduction

In the crystal structures of the drug active barbiturates such as 5,5-diethylbarbituric acid or barbital (Fig. 1), the most important molecular interactions are NH···O=C hydrogen bonds. These link molecules together to form a variety of different hydrogen-bonded frameworks which may be one-dimensional (ribbons) or two-dimensional (sheets). The structure of the drug molecules is such that the C(5) nonpolar substituents project outwards from the framework. In a barbiturate crystal structure, the most suitable framework geometry is that which can be stacked to give the most favorable packing of C(5) substituents. Three-dimensional frameworks are geometrically possible, but have not been observed for any barbiturates. Presumably, this is because the space available for C(5) substituents is completely defined by the framework, thereby imposing on them steric requirements that cannot easily be satisfied, *e.g.*, ethyl groups would be too large.

Polymorphism is found for most drug active barbiturates. In amobarbital I and II (Craven & Vizzini, 1969), both polymorphs have the same hydrogen-bonded framework and nearly the same conformation for the isoamyl groups. The crystal structures differ in the stacking mode of the frameworks. In barbital I and II (Craven, *et al.*, 1969), there are different ribbon-type frameworks; thus, the crystal structures are quite different. We now report the crystal structure determination of barbital IV, showing that this has yet a third framework which is of the sheet type.

Supposedly, six polymorphs of barbital exist. However, only I, II, III, and IV have been characterized by their crystal morphology and melting points (Köfler, 1948). The existence of V and VI has been postulated, based on phase equilibria studies of binary barbiturate systems with barbital as one component (Brandstätter-Kuhnert & Aepkers, 1963).

We have not been able to obtain barbital III by evaporating alcoholic solutions or from the melt. Köfler (1948) describes form III as fine monoclinic needles (m.p. 181°C) frequently bent, which can be grown by sublimation at about 100°C. We obtained crystals of this description, using this method, but their single-crystal X-ray diffraction patterns showed them to be form II (m.p. 183°C). Thus, sublimation yields form II in quite a different crystal habit from the many faceted monoclinic prisms grown from ethanolic solution.

Infrared spectra and X-ray powder data have been reported only for barbital I, II, and IV (Cleverley & Williams, 1959; Craven *et al.*, 1969; Huang, 1951). We suspect that form III may not exist. In a recent study of the dissolution rates of barbital polymorphs in water, Nogami, Nagai, Fukuoko & Yotsuyanagi (1969) describe a form III. However, by comparing their infrared spectrum with that of Craven *et al.* (1969) and their X-ray powder data with those of Huang (1951), this form appears to be IV.

Experimental

Pyramidal crystals of barbital IV were hand-picked from the mixture of crystals of phases I, II, and IV which was obtained by the slow evaporation of an ethanolic solution at room temperature. These monoclinic pyramids have a basal plane (010) with crystal symmetry 2, and pseudosymmetry *m*2*m*. The crystals cleave parallel to (010). Barbital IV is also commonly obtained, from ethanolic solution, as flat rectangular

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Table 1. *Observed and calculated structure amplitudes for barbital* IV

The columns are *k*, 10|F_o|, 10|F_c|. Asterisks indicate reflections which were unobservably weak and also the nine reflections that were given zero weight in the least-squares refinement.

H= 0, L=0		
2	536*	983
4	730*	1095
6	702	830
8	684	774
10	372	386
12	545	564
14	61	49
16	14*	24
18	648	676
20	200	203
22	254	251
24	41	34
H= 1, L=0		
0	26	9
1	15	13
2	47	38
3	18	16
4	36	32
5	35	31
6	26	28
7	113	122
8	55	59
9	34	33
10	24	29
11	69	71
12	28	30
13	15	13
14	26	26
15	52	51
16	15	12
17	38	34
18	51	51
19	53	57
20	32	36
21	43	47
22	9*	6
23	9*	9
24	17	10
25	19	16
H= 2, L=0		
0	7*	7
1	99	84
2	1268*	1374
3	672	717
4	681	721
5	1005*	1216
6	620	659
7	539	563
8	712	774
9	267	251
10	289	276
11	318	284
12	318	318
13	315	318
14	115	106
15	179	171
16	119	130
17	104	106
18	32	28
19	41	46
20	371	376
21	119	116
22	20	20
23	129	137
24	35	35
25	94	90
H= 3, L=0		
0	69	66
1	86	[illegible]
2	46	45
3	53	51
4	79	66
5	28	32
6	63	66
7	38	38
8	23	19
9	33	38
10	13	9
11	56	53
12	45	49
13	64	64
14	31	30
15	52	56
16	18	12
17	23	18
18	24	26
19	44	45
20	42	43
21	9*	7
22	26	30
23	13	18
24	21	22
H= 4, L=0		
0	1261*	1446
1	614	611
2	531	534
3	480	462
4	415	416
5	83	93
6	275	285
7	305	297
8	206	198
9	40	28
10	462	443
11	85	76
12	666	684
13	155	[illegible]
14	206	205
15	35	32
16	17	29
17	31	26
18	28	32
19	107	116
20	40	33
21	19	20
22	17	23
23	9*	7
H= 5, L=0		
0	58	63
1	41	46
2	46	38
3	6*	7
4	23	21
5	52	54
6	45	44
7	19	21
8	25	20
9	17	14
10	34	30
11	42	44
12	33	37
13	28	33
14	16	17
15	27	16
16	15	8
17	18	18
18	35	42
19	22	25
20	16	17
21	30	28
22	15	20
23	15	17
H= 6, L=0		
0	64	61
1	569	530
2	150	165
3	436	434
4	453	451
5	222	214
6	53	63
7	102	114
8	142	153
9	178	169
10	55	59
11	245	240
12	193	191
13	47	55
14	9*	10
15	10*	9
16	82	92
17	61	80
18	91	95
19	150	165
20	147	150
21	66	65
22	38	45
H= 7, L=0		
0	46	40
1	38	42
2	29	17
3	17	10
4	16	18
5	40	41
6	29	30
7	27	27
8	21	23
9	22	18
10	21	22
11	24	24
12	9*	7
13	18	15
14	26	[illegible]
15	9*	8
16	9*	7
17	27	21
18	28	32
19	9*	6
20	9*	8
21	15	15
H= 8, L=0		
0	86	77
1	467	459
2	266	266
3	402	390
4	325	313
5	173	165
6	64	57
7	315	318
8	53	56
9	47	45
10	111	110
11	114	114
12	91	86
13	140	156
14	182	156
15	42	47
16	206	218
17	87	93
18	108	111
19	42	46
20	28	29
H= 9, L=0		
0	9*	8
1	48	54
2	45	47
3	21	24
4	33	33
5	15	22
6	33	[illegible]
7	44	43
8	15	8
9	18	12
10	16	12
11	33	33
12	49	54
13	9*	7
14	28	23
15	26	27
16	27	30
17	9*	5
18	17	14
19	23	19
H= 10, L=0		
0	25	32
1	128	131
2	193	202
3	59	58
4	182	189
5	360	359
6	348	349
7	335	330
8	46	44
9	68	73
10	47	51
11	260	265
12	276	284
13	238	251
14	105	114
15	111	119
16	106	109
17	16	17
H= 11, L=0		
0	45	43
1	17	11
2	21	31
3	24	[illegible]
4	23	24
5	17	20
6	40	42
7	22	21
8	41	41
9	45	40
10	18	21
11	27	25
12	9*	12
13	18	21
14	21	21
15	9*	11
H= 12, L=0		
0	125	119
1	145	152
2	213	219
3	101	100
4	116	120
5	35	44
6	178	177
7	51	53
8	152	161
9	127	136
10	58	61
11	39	43
12	19	19
13	77	87
H= 13, L=0		
0	19	12
1	17	12
2	20	15
3	9*	9
4	36	40
5	18	16
6	17	17
7	16	12
8	21	11
9	16	9
H= 14, L=0		
0	20	16
1	122	128
2	46	54
3	60	96
H=-14, L=1		
0	43	41
1	39	40
H=-13, L=1		
0	9*	2
1	158	165
2	50	52
3	82	88
4	75	78
5	57	66
6	23	17
7	92	94
8	40	34
9	66	64
H=-12, L=1		
0	42	38
1	28	38
2	88	94
3	125	132
4	170	173
5	180	188
6	132	134
7	109	112
8	95	91
9	50	55
10	9*	8
11	48	53
12	65	67
H=-11, L=1		
0	98	95
1	44	47
2	85	88
3	110	114
4	95	95
5	60	57
6	158	153
7	53	56
8	42	36
9	150	162
10	94	100
11	41	43
12	30	27
13	21	14
14	160	162
15	75	76
H=-10, L=1		
0	95	93
1	36	36
2	81	80
3	140	150
4	123	124
5	38	40
6	158	161
7	294	298
8	297	295
9	246	253
10	222	224
11	146	143
12	73	76
13	121	120
14	174	180
15	134	156
16	103	112
17	39	45
H= -9, L=1		
0	30	19
1	196	191
2	53	59
3	244	252
4	136	133
5	19	23
6	119	119
7	154	161
8	71	73
9	127	124
10	109	112
11	277	288
12	42	39
13	139	144
14	19	17
15	83	89
16	40	40
17	67	69
18	42	42
H= -8, L=1		
0	274	259
1	199	159
2	128	131
3	129	122
4	93	98
5	94	95
6	55	54
7	66	63
8	166	165
9	189	183
10	152	153
11	80	80
12	134	133
13	176	179
14	129	134
15	98	99
16	156	166
17	181	[illegible]
18	121	133
19	83	87
20	56	54
H= -7, L=1		
0	67	64
1	43	55
2	72	75
3	80	78
4	104	95
5	235	232
6	162	158
7	149	140
8	82	77
9	114	122
10	97	100
11	35	34
12	18	14
13	149	149
14	124	124
15	32	28
16	75	79
17	94	97
18	22	22
19	26	34
20	52	59
21	19	30
H= -6, L=1		
0	166	166
1	206	198
2	338	311
3	396	380
4	227	215
5	134	149
6	92	93
7	139	137
8	229	229
9	205	[illegible]
10	165	160
11	28	23
12	89	86
13	98	98
14	53	44
15	42	37
16	22	16
17	88	93
18	113	111
19	155	162
20	176	188
21	111	120
22	65	74
H= -5, L=1		
0	144	132
1	495	493
2	150	142
3	393	381
4	153	133
5	359	352
6	348	329
7	247	237
8	36	32
9	70	61
10	278	255
11	61	53
12	34	36
13	163	163
14	45	55
15	51	50
16	25	25
17	31	43
18	101	104
19	59	77
20	19	13
21	109	113
22	64	67
23	20	[illegible]
H= -4, L=1		
0	175	155
1	360	357
2	304	313
3	174	179
4	88	79
5	117	110
6	127	123
7	171	164
8	302	296
9	525	512
10	410	407
11	295	280
12	109	103
13	70	61
14	94	85
15	84	81
16	85	81
17	67	66
18	36	35
19	63	70
20	68	72
21	71	72
22	64	64
23	54	47
H= -3, L=1		
0	84	93
1	854	902
2	233	218
3	121	130
4	103	106
5	271	260
6	336	346
7	390	371
8	292	293
9	195	196
10	102	[illegible]
11	220	232
12	190	184
13	284	276
14	245	237
15	145	143
16	192	193
17	43	50
18	140	139
19	120	122
20	126	129
21	121	118
22	39	41
23	74	72
24	8*	10
H= -2, L=1		
0	608	635
1	670	691
2	148	154
3	172	164
4	255	251
5	129	141
6	99	98
7	254	256
8	306	293
9	177	181
10	168	153
11	318	299
12	318	311
13	181	174
14	80	80
15	167	164
16	166	170
17	206	205
18	242	250
19	207	205
20	185	183
21	83	84
22	77	81
23	29	34
24	25	28
H= -1, L=1		
0	115	108
1	473	472
2	165	151
3	371	375
4	127	139
5	288	317
6	235	253
7	724	769
8	252	249
9	286	290
10	227	229
11	267	257
12	94	101
13	49	47
14	8*	8
15	172	173
16	108	106
17	54	55
18	102	101
19	252	254
20	48	45
21	61	60
22	27	26
23	31	31
24	77	83
H= 0, L=1		
0	61	68
1	1050*	1367
2	913*	1118
3	951*	1182
4	244	245
5	45	39
6	107	116
7	353	371
8	79	92
9	87	93
10	106	89
11	289	291
12	107	103
13	96	96
14	24	27
15	157	153
16	175	175
17	97	99
18	157	162
19	324	335
20	316	321
21	313	314
22	88	92
23	62	64
24	57	58
25	116	112
H= 1, L=1		
0	591	600
1	127	117
2	335	321
3	205	204
4	530	531
5	152	143
6	309	286
7	266	265
8	699	715
9	260	252
10	130	129
11	210	195
12	152	141
13	65	66
14	101	101
15	75	75
16	136	138
17	81	82
18	228	[illegible]
19	49	49
20	195	200
21	29	29
22	17	10
23	59	63
24	22	23
25	51	54
H= 2, L=1		
0	541	546
1	729	771
2	187	195
3	92	89
4	241	242
5	124	129
6	126	115
7	219	213
8	271	257
9	127	128
10	141	135
11	337	314
12	269	257
13	125	121
14	81	78
15	152	138
16	201	201
17	278	286
18	228	235
19	220	228
20	184	183
21	114	114
22	101	103
23	25	27
24	22	24
25	32	46
H= 3, L=1		
0	53	52
1	299	300
2	818	863
3	187	196
4	400	384
5	198	194
6	232	222
7	386	370
8	93	87
9	111	116
10	86	82
11	154	144
12	371	375
13	214	209
14	81	80
15	274	281
16	42	43
17	25	20
18	55	57
19	153	160
20	211	222
21	9*	11
22	32	30
23	41	43
24	25	29
H= 4, L=1		
0	291	272
1	384	391
2	220	224
3	155	168
4	56	49
5	131	123
6	87	85
7	125	122
8	260	247
9	575	562
10	370	363
11	347	339
12	137	136
13	101	[illegible]
14	141	145
15	56	58
16	61	59
17	50	51
18	33	38
19	74	81
20	74	73
21	87	92
22	74	78
23	47	45
H= 5, L=1		
0	792	800
1	160	148
2	194	192
3	239	218
4	123	114
5	303	287
6	465	453
7	205	191
8	24	28
9	253	249
10	124	117
11	152	151
12	66	61
13	120	123
14	157	157
15	9*	11
16	20	10
17	50	53
18	99	110
19	75	75
20	49	45
21	88	91
22	70	94
23	46	52
H= 6, L=1		
0	111	[illegible]
1	174	173
2	400	376
3	429	413
4	170	165
5	231	213
6	98	97
7	153	156
8	183	182
9	132	121
10	187	177
11	21	14
12	83	82
13	73	66
14	54	45
15	42	42
16	62	56
17	107	114
18	72	72
19	156	160
20	166	174
21	83	93
22	81	88
H= 7, L=1		
0	27	22
1	44	48
2	22	33
3	49	50
4	148	143
5	138	127
6	209	208
7	56	54
8	130	127
9	23	26
10	57	68
11	59	51
12	111	107
13	130	135
14	80	[illegible]
15	31	32
16	92	90
17	71	74
18	53	52
19	30	28
20	34	40
21	9*	15
H= 8, L=1		
0	343	347
1	127	128
2	86	91
3	80	81
4	66	63
5	130	133
6	124	128
7	34	32
8	217	212
9	198	196
10	170	171
11	61	59
12	139	141
13	175	179
14	191	292
15	81	86
16	99	108
17	181	189
18	103	116
19	53	59
20	59	63
H= 9, L=1		
0	339	333
1	83	80
2	94	93
3	110	115
4	169	165
5	124	124
6	68	71
7	71	72
8	252	252
9	173	181
10	100	100
11	147	152
12	226	228
13	54	58
14	47	54
15	9*	6
16	67	70
17	65	70
18	41	45
H= 10, L=1		
0	9*	3
1	26	25
2	29	31
3	93	101
4	119	121
5	9*	5
6	128	138
7	287	295
8	316	324
9	147	145
10	226	228
11	110	111
12	94	95
13	172	180
14	105	113
15	196	205
16	49	43
17	15	22
H= 11, L=1		
0	36	36
1	114	117
2	49	54
3	65	71
4	114	120
5	145	143
6	94	99
7	79	77
8	19	18
9	80	86
10	92	96
11	55	35
12	36	39
13	161	172
14	105	111
15	72	82
H= 12, L=1		
0	23	31
1	36	41
2	89	93
3	42	37
4	119	122
5	192	196
6	96	100
7	156	165
8	102	104
9	20	23
10	26	24
11	70	78
12	69	81
H= 13, L=1		
0	140	141
1	68	69
2	120	110
3	46	48
4	39	42
5	58	65
6	101	110
7	81	88
8	115	115
9	28	31
H=-13, L=2		
0	28	30
1	54	52
2	114	123
3	97	102
4	139	153
5	86	87
6	72	71
7	25	25
H=-12, L=2		
0	31	36
1	98	103
2	18	16
3	83	83
4	48	48
5	129	135
6	23	16
7	49	45
8	17	23
9	14	11
10	31	32
11	48	53
H=-11, L=2		
0	74	82
1	100	95
2	146	145
3	161	167
4	79	71
5	20	20
6	35	33
7	56	60
8	57	62
9	36	44
10	78	83
11	92	95
12	71	73
13	55	61
14	43	45
H=-10, L=2		
0	29	30
1	10*	12
2	68	65
3	146	142
4	74	80
5	228	232
6	38	39
7	41	42
8	45	45
9	107	112
10	73	79
11	61	63
12	76	74
13	154	160
14	45	47
15	31	35
16	15	20
H= -9, L=2		
0	35	35
1	97	95
2	186	181
3	66	60
4	64	71
5	43	45
6	52	59
7	160	162
8	216	220
9	190	195
10	311	329
11	124	124
12	32	30
13	23	27
14	34	41
15	9*	11
16	54	[illegible]
17	62	62
18	77	79
H= -8, L=2		
0	9*	3
1	117	122
2	127	134
3	204	195
4	54	50
5	43	45
6	121	115
7	205	212
8	227	239
9	100	104
10	263	268
11	260	268
12	88	90
13	22	26
14	30	32
15	73	79
16	34	38
17	63	63
18	61	59
19	15	12
H= -7, L=2		
0	205	191
1	133	123
2	142	140
3	64	58
4	122	129
5	85	86
6	182	182
7	79	81
8	93	98
9	57	60
10	147	151
11	107	103
12	182	151
13	80	81
14	36	43
15	72	73
16	46	46
17	22	25
18	18	24
19	16	17
20	25	27
H= -6, L=2		
0	600	569
1	288	269
2	300	280
3	531	531
4	140	128
5	232	220
6	64	57
7	123	125
8	111	103
9	52	51
10	81	78
11	35	32
12	78	80
13	64	63
14	71	72
15	181	189
16	69	77
17	88	91
18	94	100
19	36	39
20	26	28
21	16	16
H= -5, L=2		
0	73	75
1	229	225
2	533	520
3	280	283
4	414	[illegible]
5	245	238
6	186	179
7	299	287
8	364	363
9	85	79
10	53	54
11	47	42
12	70	75
13	57	53
14	48	45
15	107	108
16	49	44
17	26	30
18	15	19
19	47	53
20	126	142
21	75	76
22	9*	10
H= -4, L=2		
0	62	69
1	227	211
2	495	475
3	466	454
4	146	137
5	297	285
6	151	146
7	106	111
8	202	198
9	206	194
10	294	303
11	217	220
12	139	125
13	52	34
14	22	28
15	44	42
16	52	55
17	30	35
18	79	[illegible]
19	35	29
20	16	19
21	38	44
22	31	31
H= -3, L=2		
0	965	987
1	645	650
2	293	273
3	277	264
4	158	167
5	151	152
6	167	160
7	139	135
8	395	393
9	513	514
10	193	194
11	131	124
12	111	114
13	46	45
14	164	165
15	42	42
16	100	107
17	266	267
18	234	250
19	71	77
20	67	72
21	117	120
22	117	123
23	76	75
H= -2, L=2		
0	1090	1158
1	450	451
2	925	928
3	699	689
4	328	319
5	266	270
6	268	263
7	196	182
8	77	87
9	385	373
10	304	284
11	104	102
12	207	201
13	145	140
14	127	131
15	241	241
16	111	124
17	92	85
18	84	76
19	76	68
20	25	23
21	38	34
22	34	35
23	48	49
H= -1, L=2		
0	177	178
1	269	262
2	359	346
3	886	945
4	923	970
5	391	399
6	399	408
7	190	189
8	392	382
9	173	166
10	97	92
11	534	523
12	164	167
13	44	47
14	33	36
15	136	98
16	109	111
17	92	93
18	77	69
19	136	[illegible]
20	100	102
21	77	80
22	114	109
23	68	64
H= 0, L=2		
0	35	43
1	451	458
2	398	403
3	794	855
4	222	230
5	164	150
6	183	186
7	803	807
8	407	391
9	387	359
10	166	184
11	441	460
12	103	105
13	129	133
14	114	110
15	64	62
16	110	100
17	296	289
18	62	63
19	21	14
20	10*	14
21	70	72
22	17	22
23	71	79
24	14	7
H= 1, L=2		
0	680	678
1	157	160
2	535	522
3	724	736
4	693	733
5	763	[illegible]
6	139	132
7	162	148
8	340	331
9	344	350
10	136	132
11	145	151
12	243	237
13	84	88
14	34	31
15	54	56
16	122	122
17	130	135
18	85	80
19	41	46
20	68	54
21	122	127
22	125	132
23	95	96
24	62	64
H= 2, L=2		
0	1088	1139
1	547	536
2	917	923
3	679	673
4	330	317
5	179	195
6	319	312
7	182	171
8	125	133
9	479	466
10	330	325
11	100	92
12	214	211
13	173	171
14	148	147
15	219	221
16	130	137
17	107	[illegible]
18	90	88
19	89	88
20	38	34
21	49	48
22	42	42
23	19	19
24	24	24
H= 3, L=2		
0	313	314
1	733	749
2	653	629
3	451	429
4	53	62
5	221	216
6	68	65
7	194	192
8	347	331
9	220	212
10	318	313
11	246	243
12	57	57
13	100	104
14	85	81
15	83	81
16	133	129
17	147	167
18	188	193
19	216	232
20	104	107
21	92	94
22	19	15
23	54	59
24	54	61
H= 4, L=2		
0	34	45
1	129	124
2	380	[illegible]
3	523	501
4	265	238
5	281	268
6	214	206
7	171	175
8	200	194
9	249	234
10	212	211
11	184	173
12	159	157
13	31	30
14	17	17
15	26	18
16	68	75
17	39	42
18	50	50
19	44	40
20	26	29
21	44	45
22	15	18
H= 5, L=2		
0	38	26
1	646	615
2	269	268
3	36	37
4	86	88
5	325	308
6	255	262
7	500	495
8	133	120
9	162	169
10	88	85
11	63	65
12	25	27
13	40	42
14	103	99
15	57	57
16	41	[illegible]
17	52	37
18	35	37
19	122	133
20	45	51
21	82	90
22	14	13
H= 6, L=2		
0	462	432
1	283	269
2	379	369
3	486	481
4	271	262
5	255	249
6	41	37
7	165	166
8	165	165
9	74	74
10	52	52
11	19	13
12	99	99
13	107	119
14	100	98
15	159	168
16	121	126
17	96	104
18	60	68
19	25	26
20	28	30
21	8*	10
H= 7, L=2		
0	43	42
1	175	166
2	92	93
3	8*	10
4	53	58
5	162	165
6	43	33
7	163	164
8	56	59
9	44	50
10	46	45
11	241	242
12	132	136
13	168	177
14	52	47
15	37	37
16	69	75
17	18	22
18	31	33
19	31	38
20	27	27
H= 8, L=2		
0	35	39
1	159	149
2	162	163
4	113	115
5	71	67
6	81	75
7	165	171
8	224	231
9	205	214
10	292	303
11	209	215
12	83	83
13	16	21
14	57	56
15	42	45
16	22	19
17	62	64
18	73	80
19	25	28
H= 9, L=2		
0	126	110
1	175	[illegible]
2	60	62
3	92	82
4	22	22
5	55	54
6	99	107
7	65	68
8	92	88
9	295	294
10	142	152
11	178	187
12	61	61
13	46	43
14	32	35
15	62	77
16	35	31
17	75	80
H= 10, L=2		
0	33	37
1	37	38
2	93	100
3	128	123
4	128	125
5	203	210
6	116	123
7	50	52
8	45	47
9	81	85
10	87	88
11	83	92
12	116	121
13	95	106
14	45	48
15	9*	12
16	8*	7
H= 11, L=2		
0	25	29
1	89	103
2	134	135
3	104	100
4	106	103
5	24	25
6	75	72
7	21	24
8	26	30
9	32	33
10	25	24
11	19	20
12	146	156
13	30	25
14	54	51
H= 12, L=2		
0	75	80
1	84	83
2	18	21
3	65	64
4	95	98
5	122	126
6	64	69
7	31	29
8	15	16
9	17	25
10	22	19
11	28	27
H= 13, L=2		
0	63	67
1	84	90
2	56	60
3	138	147
4	59	64
5	137	112
6	79	89
H=-13, L=3		
0	96	110
1	75	73
2	76	80
H=-12, L=3		
0	9*	15
1	32	32
2	110	118
3	45	44
4	58	57
5	84	86
6	25	31
7	30	31
8	94	93
9	47	46
H=-11, L=3		
0	9*	11
1	25	31
2	82	97
3	96	99
4	84	89
5	58	54
6	80	82
7	36	62
8	47	51
9	22	25
10	46	47
11	56	59
12	36	38
H=-10, L=3		
0	85	96
1	60	62
2	15	17
3	112	108
4	73	75
5	183	183
6	93	94
7	46	41
8	89	91
9	29	23
10	38	38
11	9*	12
12	31	30
13	25	24
14	20	18
H= -9, L=3		
0	10*	1
1	9*	12
2	39	42
3	34	37
4	60	59
5	15	14
6	76	77
7	65	69
8	10*	17
9	47	49
10	145	149
11	132	133
12	135	166
13	78	85
14	64	69
15	45	46
16	56	63
H= -8, L=3		
0	66	65
1	136	138
2	17	21
3	141	139
4	57	51
5	213	214
6	94	91
7	40	45
8	308	303
9	157	160
10	255	[illegible]
11	206	208
12	88	90
13	57	51
14	45	41
15	90	93
16	30	29
17	131	129
18	45	49
H= -7, L=3		
0	20	20
1	68	70
2	95	93
3	104	103
4	117	117
5	71	69
6	54	59
7	40	48
8	262	272
9	247	251
10	323	332
11	92	94
12	44	54
13	68	63
14	110	112
15	44	47
16	84	86
17	56	59
18	60	61
19	9*	11
H= -6, L=3		
0	49	28
1	51	50
2	279	244
3	125	122
4	51	46
5	140	131
6	194	[illegible]
7	203	200
8	45	46
9	173	171
10	344	345
11	145	143
12	138	133
13	203	196
14	97	99
15	109	118
16	167	177
17	83	82
18	62	67
19	98	97
20	31	27
H= -5, L=3		
0	350	333
1	173	163
2	148	142
3	45	37
4	64	70
5	60	60
6	129	126
7	97	92
8	70	73
9	20	22
10	87	93
11	158	163
12	112	112
13	162	162
14	56	55
15	69	67
16	75	76
17	138	147
18	75	102
19	18	26
20	20	22
21	9*	9
H= -4, L=3		
0	20	14
1	144	139
2	279	277
3	110	110
4	318	314
5	93	88
6	63	58
7	123	132
8	124	129
9	52	50
10	174	177
11	49	50
12	41	41
13	246	251
14	72	74
15	200	199
16	137	150
17	49	45
18	174	174
19	24	26
20	62	68
21	16	14
H= -3, L=3		
0	112	113
1	213	209
2	448	461
3	292	308
4	321	334
5	197	199
6	118	118
7	63	63
8	114	119
9	171	180
10	90	91
11	58	53
12	39	32
13	80	[illegible]
14	142	140
15	205	208
16	185	186
17	69	75
18	31	33
19	71	72
20	107	114
21	101	106
22	65	62
H= -2, L=3		
0	91	86
1	104	114
2	55	69
3	220	232
4	216	227
5	262	267
6	74	76
7	78	87
8	27	19
9	178	168
10	245	242
11	252	259
12	31	29
13	88	79
14	127	128
15	78	74
16	74	66
17	49	59
18	47	42
19	83	88
20	39	42
21	65	61
22	43	42
H= -1, L=3		
0	122	135
1	127	153
2	212	[illegible]
3	143	158
4	91	90
5	153	153
6	187	195
7	257	254
8	174	172
9	212	218
10	112	108
11	53	55
12	99	99
13	85	92
14	118	120
15	78	87
16	116	115
17	83	86
18	90	97
19	60	57
20	36	35
21	15	9
22	37	36
H= 0, L=3		
0	7*	2
1	55	57
2	249	261
3	39	41
4	142	125
5	83	81
6	489	473
7	48	50
8	66	63
9	89	88
10	435	412
11	68	74
12	99	96
13	28	36
14	56	59
15	51	51
16	156	[illegible]
17	59	59
18	217	213
19	24	23
20	55	53
21	9*	4
22	54	55
23	8*	6
H= 1, L=3		
0	99	102
1	199	202
2	255	261
3	212	200
4	103	94
5	187	184
6	242	249
7	169	174
8	176	176
9	115	110
10	84	89
11	52	49
12	81	80
13	113	114
14	75	71
15	130	122
16	122	120
17	110	113
18	26	30
19	53	61
20	52	46
21	19	18
22	78	77
23	80	76
H= 2, L=3		
0	32	32
1	102	103
2	75	80
3	267	[illegible]
4	229	236
5	264	256
6	30	27
7	64	76
8	133	129
9	224	121
10	258	252
11	278	275
12	48	41
13	101	93
14	114	117
15	116	112
16	48	49
17	51	56
18	31	24
19	86	95
20	37	33
21	65	71
22	25	22
23	158	162
H= 3, L=3		
0	10*	1
1	286	282
2	372	374
3	421	413
4	287	297
5	242	241
6	61	62
7	79	87
8	164	157
9	128	127
10	152	154
11	66	63
12	28	25
13	65	62
14	191	201
15	194	205
16	130	[illegible]
17	68	78
18	53	51
19	81	89
20	103	110
21	114	117
22	92	104
H= 4, L=3		
0	27	25
1	27	24
2	306	288
3	31	33
4	253	255
5	127	129
6	8*	13
7	122	127
8	174	180
9	29	33
10	199	200
11	80	64
12	64	69
13	195	202
14	103	103
15	232	235
16	154	151
17	33	31
18	147	148
19	16	13
20	45	53
21	30	27
H= 5, L=3		
0	273	264
1	283	270
2	118	115
3	57	54
4	56	54
5	51	46
6	84	[illegible]
7	107	113
8	87	87
9	22	28
10	139	144
11	190	203
12	161	164
13	74	73
14	76	77
15	84	83
16	108	105
17	69	98
18	67	73
19	43	45
20	22	21
21	26	29
H= 6, L=3		
0	8*	8
1	69	78
2	223	208
3	143	139
4	39	46
5	101	98
6	155	150
7	219	214
8	15	11
9	210	203
10	294	285
11	171	180
12	135	136
13	210	204
14	44	41
15	155	166
16	122	127
17	78	81
18	39	48
19	105	110
20	37	40
H= 7, L=3		
0	59	64
1	50	44
2	83	81
3	90	91
4	88	85
5	91	88
6	80	76
7	91	98
8	227	235
9	319	324
10	303	312
11	182	184
12	22	19
13	80	81
14	101	104
15	78	83
16	64	70
17	46	51
18	48	46
19	52	52
H= 8, L=3		
0	32	34
1	94	90
2	72	76
4	92	90
5	242	240
6	46	48
7	67	70
8	300	301
9	91	86
10	161	157
11	242	243
12	32	44
13	42	39
14	74	74
15	95	101
16	26	[illegible]
17	132	131
H= 9, L=3		
0	21	12
1	29	37
2	59	71
3	63	71
4	53	58
5	57	64
6	55	55
7	53	61
8	61	64
9	43	44
10	53	84
11	113	117
12	97	100
13	92	96
14	45	30
15	26	28
16	49	46
H= 10, L=3		
0	137	145
1	47	46
2	18	23
3	129	131
4	56	62
5	172	177
6	110	107
7	10*	13
8	91	97
9	25	18
10	51	51
11	9*	10
12	43	41
13	9*	5
14	8*	8
H= 11, L=3		
0	30	31
1	28	30
2	61	69
3	89	99
4	88	92
5	78	84
6	84	91
7	67	74
8	18	22
9	33	33
10	49	51
11	50	51
H= 12, L=3		
0	9*	4
1	35	37
2	89	93
3	9*	9
4	47	48
5	77	81
6	26	34
7	9*	9
8	90	97
H=-12, L=4		
0	27	36
1	15	18
2	27	23
3	44	42
H=-11, L=4		
0	21	22
1	124	138
2	30	26
3	32	25
4	101	109
5	9*	8
6	9*	10
7	81	[illegible]
8	78	86
9	15	13
H=-10, L=4		
0	16	17
1	31	37
2	57	66
3	54	58
4	52	57
5	50	52
6	38	41
7	74	77
8	69	65
9	47	53
10	38	41
11	32	29
12	9*	7
H= -9, L=4		
0	49	53
1	82	90
2	10*	14
3	58	64
4	28	27
5	20	22
6	46	38
7	116	121
8	33	36
9	86	95
10	9*	10
11	32	37
12	9*	12
13	14	13
14	34	31
H= -8, L=4		
0	44	52
1	36	37
2	74	[illegible]
3	138	132
4	108	112
5	62	62
6	49	43
7	66	65
8	37	39
9	43	42
10	100	101
11	80	86
12	48	32
13	9*	14
14	53	54
15	71	70
H= -7, L=4		
0	21	19
1	151	143
2	29	50
3	28	24
4	24	24
5	202	205
6	22	18
7	296	298
8	73	76
9	21	15
10	62	66
11	244	244
12	26	29
13	94	98
14	30	23
15	19	22
16	33	32
17	30	25
H= -6, L=4		
0	97	94
1	123	120
2	61	64
3	53	[illegible]
4	68	63
5	30	25
6	113	114
7	211	218
8	286	287
9	282	290
10	217	218
11	88	87
12	20	25
13	105	110
14	92	94
15	22	22
16	51	52
17	74	74
18	60	62
H= -5, L=4		
0	134	121
1	49	43
2	160	147
3	193	198
4	70	46
5	90	92
6	109	101
7	181	178
8	94	98
9	94	100
10	96	98
11	10*	10
12	10*	10
13	72	70
14	163	168
15	112	115
16	38	41
17	22	21
18	9*	4
19	49	30
H= -4, L=4		
0	144	139
1	147	143
2	218	216
3	257	253
4	286	307
5	299	301
6	206	210
7	82	77
8	150	152
9	153	156
10	51	47
11	107	110
12	153	156
13	112	115
14	110	115
15	41	36
16	24	27
17	31	31
18	9*	5
19	19	21
20	25	23
H= -3, L=4		
0	15	10
1	265	273
2	147	156
3	59	60
4	9*	11
5	397	428
6	281	294
7	176	181
8	34	34
9	36	50
10	207	200
11	32	38
12	238	244
13	162	162
14	19	13
15	16	[illegible]
16	104	110
17	161	169
18	92	101
19	59	66
20	9*	12
H= -2, L=4		
0	83	81
1	146	164
2	170	204
3	203	236
4	232	257
5	171	178
6	129	130
7	43	45
8	43	43
9	114	112
10	65	62
11	32	32
12	73	64
13	61	59
14	10*	15
15	54	56
16	78	80
17	47	42
18	23	16
19	33	34
20	31	30
H= -1, L=4		
0	177	195
1	51	62
2	25	22
3	150	177
4	239	207
5	89	94
6	234	245
7	390	198
8	155	151
9	222	224
10	36	26
11	65	64
12	9*	8
13	47	43
14	145	143
15	10*	4
16	79	91
17	74	67
18	43	49
19	27	31
20	60	63
21	22	18
H= 0, L=4		
0	7*	79
1	23	27
2	148	147
3	250	257
4	127	126
5	20	24
6	40	37
7	148	143
8	169	158
9	180	186
10	24	23
11	73	79
12	67	62
13	9*	1
14	41	39
15	41	43
16	49	50
17	9*	12
18	41	47
19	24	32
20	17	20
21	8*	7
H= 1, L=4		
0	44	41
1	88	86
2	190	181
3	44	49
4	105	100
5	346	352
6	70	70
7	48	48
8	224	234
9	142	145
10	182	181
11	88	87
12	24	28
13	104	102
14	40	41
15	93	83
16	21	18
17	111	117
18	77	83
19	9*	9
20	31	58
21	62	63
H= 2, L=4		
0	63	67
1	174	172
2	248	245
3	219	219
4	234	229
5	158	157
6	138	139
7	96	100
8	73	64
9	117	114
10	82	74
11	9*	16
12	61	67
13	72	70
14	21	[illegible]
15	59	82
16	98	98
17	41	45
18	38	40
19	20	19
20	15	18
21	56	57
H= 3, L=4		
0	207	203
1	115	112
2	287	281
3	131	130
4	211	214
5	202	193
6	381	376
7	91	98
8	78	71
9	211	210
10	88	97
11	56	59
12	70	74
13	162	157
14	148	157
15	78	83
16	164	179
17	37	34
18	98	118
19	68	76
20	35	35
21	42	43
H= 4, L=4		
0	120	125
1	146	140
2	203	195
3	320	306
4	365	370
5	259	[illegible]
6	153	152
7	17	17
8	107	104
9	97	98
10	41	44
11	33	34
12	90	88
13	105	109
14	111	118
15	66	64
16	9*	7
17	9*	5
18	9*	9
19	19	19
H= 5, L=4		
0	26	22
1	160	145
2	84	91
3	72	71
4	303	299
5	73	69
6	162	161
7	68	66
8	43	38
9	64	88
10	161	162
11	39	40
12	125	124
13	96	100
14	51	52
15	74	76
16	80	86
17	38	38
18	54	55
19	8*	8
H= 6, L=4		
0	156	[illegible]
1	119	117
2	79	77
3	106	104
4	88	96
5	80	72
6	215	223
7	247	246
8	220	217
9	239	238
10	166	169
11	106	102
12	59	61
13	54	57
14	84	86
15	40	44
16	52	51
17	90	95
18	37	40
H= 7, L=4		
0	177	183
1	34	32
2	56	53
3	29	30
4	91	100
5	24	24
6	246	250
7	66	66
8	185	187
9	43	42
10	179	185
11	47	45
12	191	199
13	32	30
14	22	26
15	9*	13
16	36	31
17	25	23
H= 8, L=4		
0	36	45
1	48	52
2	128	132
3	110	102
4	105	99
5	54	34
6	46	42
7	57	63
8	17	15
9	55	59
10	57	62
11	85	92
12	46	45
13	40	41
14	60	58
15	65	66
H= 9, L=4		
0	55	37
1	53	55
2	92	92
3	44	49
4	19	7
5	25	26
6	76	80
7	51	44
8	116	125
9	24	27
10	19	22
11	9*	10
12	9*	10
13	20	21
H= 10, L=4		
0	9*	12
1	42	48
2	45	49
3	67	77
4	28	27
5	30	26
6	60	64
7	69	74
8	78	79
9	62	61
10	43	48
11	23	27
H= 11, L=4		
0	154	162
1	50	34
2	67	73
3	69	69
4	39	39
5	53	60
6	44	45
7	61	62
8	68	70
H=-10, L=5		
0	9*	1
1	73	89
2	25	25
3	47	51
4	29	28
5	9*	10
6	27	31
7	51	52
H= -9, L=5		
0	95	97
1	44	52
2	65	47
3	75	86
4	55	37
5	19	17
6	42	44
7	15	[illegible]
8	72	74
9	50	51
10	28	29
H= -8, L=5		
0	125	124
1	79	75
2	24	26
3	74	78
4	57	58
5	69	69
6	29	26
7	113	116
8	127	129
9	50	35
10	41	42
11	38	41
12	38	39
H= -7, L=5		
0	10*	13
1	29	27
2	48	50
3	26	35
4	99	95
5	49	48
6	21	21
7	48	54
8	86	89
9	55	53
10	30	30
11	56	52
12	41	38
13	69	75
14	42	40
H= -6, L=5		
0	10*	16
1	35	[illegible]
2	114	110
3	40	40
4	118	120
5	187	185
6	110	116
7	168	168
8	33	33
9	33	30
10	28	32
11	124	127
12	78	75
13	226	235
14	72	74
15	243	149
H= -5, L=5		
0	23	21
1	18	5
2	54	58
3	51	55
4	29	38
5	54	53
6	30	28
7	56	58
8	113	117
9	91	92
10	38	36
11	18	19
12	10*	10
13	58	56
14	61	59
15	70	72
16	30	24
H= -4, L=5		
0	28	22
1	9*	10
2	171	142
3	43	[illegible]
4	132	141
5	52	53
6	191	194
7	158	173
8	205	217
9	121	125
10	18	13
11	49	44
12	86	85
13	66	62
14	39	40
15	72	77
16	55	56
17	25	27
H= -3, L=5		
0	41	52
1	43	56
2	9*	11
3	65	70
4	128	139
5	32	34
6	110	123
7	139	148
8	66	68
9	16	17
10	64	61
11	46	44
12	67	69
13	100	102
14	69	78
15	46	48
16	47	53
17	35	41
18	25	27
H= -2, L=5		
0	32	33
1	149	[illegible]
2	70	78
3	109	115
4	26	24
5	41	40
6	44	49
7	91	100
8	10*	4
9	40	39
10	26	28
11	9*	7
12	76	80
13	71	76
14	40	40
15	36	34
16	144	146
17	67	74
18	73	72
H= -1, L=5		
0	34	36
1	27	32
2	33	32
3	81	93
4	31	36
5	44	39
6	62	65
7	101	96
8	65	65
9	23	22
10	92	100
11	72	75
12	24	19
13	10*	8
14	46	53
15	59	71
16	73	73
17	15	13
18	9*	2
H= 0, L=5		
0	9*	2
1	36	37
2	36	31
3	125	126
4	38	31
5	48	54
6	32	33
7	74	76
8	40	33
9	30	32
10	16	11
11	83	87
12	22	14
13	118	118
14	50	52
15	97	102
16	9*	11
17	38	33
18	18	17
19	21	26
H= 1, L=5		
0	9*	2
1	22	17
2	58	57
3	48	45
4	50	54
5	9*	3
6	45	40
7	90	91
8	85	89
9	30	35
10	72	79
11	73	79
12	23	21
13	42	51
14	47	49
15	38	[illegible]
16	51	55
17	59	61
18	9*	7
19	18	16
H= 2, L=5		
0	15	17
1	120	116
2	79	81
3	124	129
4	22	17
5	55	56
6	69	62
7	90	91
8	36	40
9	20	15
10	26	29
11	20	24
12	92	102
13	60	60
14	10*	14
15	33	35
16	146	156
17	70	72
18	68	75
19	29	38
H= 3, L=5		
0	126	132
1	32	28
2	62	68
3	110	110
4	84	90
5	35	37
6	136	140
7	131	131
8	27	20
9	105	103
10	69	[illegible]
11	26	26
12	44	45
13	45	43
14	50	52
15	81	88
16	9*	10
17	16	15
18	17	16
H= 4, L=5		
0	33	29
1	64	62
2	193	189
3	102	107
4	117	116
5	141	146
6	196	201
7	161	165
8	164	169
9	61	58
10	9*	4
11	31	28
12	70	65
13	38	35
14	24	28
15	53	49
16	66	63
17	33	33
H= 5, L=5		
0	9*	5
1	10*	7
2	50	48
3	60	59
4	144	154
5	77	73
6	17	10
7	70	61
8	137	[illegible]
9	69	73
10	28	28
11	35	27
12	9*	6
13	50	49
14	77	81
15	32	35
16	66	66
H= 6, L=5		
0	15	14
1	82	78
2	90	86
3	43	48
4	173	178
5	179	182
6	122	125
7	102	103
8	51	54
9	15	17
10	9*	12
11	95	103
12	60	60
13	197	204
14	118	123
15	148	155
H= 7, L=5		
0	16	15
1	60	60
2	30	29
3	9*	5
4	17	14
5	66	63
6	9*	11
7	62	64
8	63	64
9	38	39
10	9*	1
11	30	31
12	51	48
13	32	30
H= 8, L=5		
0	96	97
1	50	51
2	19	16
3	58	65
4	43	44
5	67	70
6	50	50
7	76	77
8	108	110
9	55	62
10	42	41
11	54	59
12	45	45
H= 9, L=5		
0	23	18
1	69	76
2	57	62
3	112	115
4	59	63
5	40	43
6	9*	12
7	9*	9
8	35	38
9	70	72
H= 10, L=5		
0	22	18
1	63	75
2	22	22
3	40	40
4	23	23
5	9*	8
H= -8, L=6		
0	45	64
1	46	47
2	18	20
3	9*	16
4	9*	6
5	19	22
6	9*	6
H= -7, L=6		
0	130	127
1	46	48
2	9*	13
3	39	38
4	71	65
5	30	28
6	51	49
7	44	49
8	60	59
9	34	33
H= -6, L=6		
0	10*	2
1	10*	15
2	19	14
3	44	42
4	46	46
5	23	25
6	78	80
7	91	93
8	94	98
9	47	48
10	71	73
11	65	63
H= -5, L=6		
0	45	47
1	99	92
2	38	[illegible]
3	27	27
4	71	62
5	168	166
6	82	85
7	108	117
8	32	42
9	9*	10
10	40	44
11	70	74
12	44	48
H= -4, L=6		
0	71	75
1	38	38
2	49	50
3	28	28
4	72	70
5	112	115
6	112	112
7	104	113
8	44	46
9	44	44
10	59	65
11	31	30
12	72	75
13	95	93
H= -3, L=6		
0	147	151
1	77	81
2	97	104
3	41	42
4	26	28
5	32	34
6	32	50
7	35	37
8	51	52
9	10*	11
10	25	[illegible]
11	31	31
12	28	26
13	9*	7
14	15	14
H= -2, L=6		
0	9*	5
1	10*	4
2	26	32
3	111	126
4	106	123
5	107	114
6	43	47
7	10*	20
8	10*	12
9	10*	7
10	66	65
11	51	55
12	77	81
13	62	61
14	33	35
15	82	80
H= -1, L=6		
0	31	27
1	45	50
2	82	92
3	41	41
4	29	30
5	79	85
6	78	81
7	55	61
8	22	24
9	26	24
10	19	12
11	20	19
12	37	40
13	26	26
14	9*	[illegible]
15	24	26
H= 0, L=6		
0	102	107
1	53	52
2	85	84
3	24	17
4	57	50
5	54	56
6	186	190
7	53	59
8	69	70
9	10*	4
10	17	11
11	9*	5
12	10*	10
13	9*	7
14	51	50
15	27	27
16	90	90
H= 1, L=6		
0	10*	5
1	88	86
2	71	73
3	55	56
4	27	30
5	64	69
6	85	93
7	35	39
8	44	46
9	19	15
10	32	35
11	45	48
12	20	22
13	14	9
14	9*	10
15	18	20
16	25	[illegible]
H= 2, L=6		
0	9*	2
1	24	22
2	64	60
3	74	72
4	137	141
5	171	173
6	10*	12
7	28	26
8	20	20
9	35	32
10	37	32
11	85	88
12	45	41
13	89	96
14	51	54
15	66	72
H= 3, L=6		
0	31	30
1	98	99
2	96	93
3	105	103
4	36	38
5	36	27
6	54	53
7	71	72
8	18	18
9	9*	6
10	21	18
11	27	28
12	20	21
13	23	20
14	14	9
15	8*	9
H= 4, L=6		
0	47	[illegible]
1	34	35
2	66	68
3	22	22
4	96	95
5	143	147
6	95	94
7	105	104
8	27	25
9	75	80
10	45	48
11	9*	17
12	35	34
13	93	92
H= 5, L=6		
0	100	97
1	65	64
2	54	59
3	71	66
4	91	88
5	87	89
6	122	128
7	65	71
8	62	66
9	15	15
10	44	45
11	58	58
12	94	96
H= 6, L=6		
0	9*	5
1	9*	9
2	9*	7
3	40	38
4	20	20
5	57	61
6	92	96
7	81	92
8	81	[illegible]
9	27	33
10	43	45
H= 7, L=6		
0	72	73
1	74	74
2	19	19
3	32	31
4	41	41
5	62	62
6	39	40
7	56	59
8	35	36
H= 8, L=6		
0	9*	7
1	49	47
2	20	21
3	9*	10
4	40	44
5	20	20
H= -5, L=7		
0	9*	7
1	9*	2
2	46	49
3	52	53
4	38	40
5	9*	4
H= -4, L=7		
0	41	39
1	40	40
2	25	23
3	31	35
4	53	57
5	48	55
6	9*	7
7	32	[illegible]
H= -3, L=7		
0	9*	15
1	27	29
2	22	23
3	62	72
4	39	45
5	97	113
6	49	53
7	9*	8
8	9*	8
H= -2, L=7		
0	23	15
1	43	48
2	63	69
3	46	47
4	28	33
5	57	59
6	47	74
7	52	55
8	24	26
9	21	19
H= -1, L=7		
0	10*	16
1	9*	13
2	9*	4
3	77	85
4	21	26
5	34	36
6	32	33
7	40	45
8	15	15
9	24	28
H= 0, L=7		
0	21	22
1	9*	[illegible]
2	10*	18
3	24	21
4	41	46
5	27	26
6	21	22
7	10*	11
8	39	23
9	27	30
H= 1, L=7		
0	9*	7
1	33	32
2	53	52
3	17	17
4	25	14
5	51	53
6	48	50
7	15	16
8	8*	7
9	19	22
10	13	15
11	8*	4
H= 2, L=7		
0	17	11
1	41	43
2	64	60
3	33	30
4	9*	8
5	64	67
6	71	74
7	42	42
8	9*	6
9	21	24
10	9*	17
H= 3, L=7		
0	16	15
1	23	[illegible]
2	25	32
3	51	50
4	108	111
5	22	21
6	28	34
7	9*	21
8	8*	5
9	13	11
H= 4, L=7		
0	50	58
1	25	27
2	17	15
3	44	46
4	71	72
5	39	38
6	8*	8
H= 5, L=7		
0	8*	15
1	35	38
2	43	45
3	36	39

Table 2. *Atomic positional and thermal parameters for barbital* IV

For each atom, corresponding parameters for the four crystallographically independent molecules are listed vertically in the order *A*, *B*, *C*, *D*. Numbers in parentheses are e.s.d.'s and refer to the least significant digits in the parameter value. Positional parameters are given as fractions of the lattice translations. The *y* parameter for atom N(1*A*) was fixed in order to define the crystallographic origin.

(*a*) Carbon, nitrogen, and oxygen atoms

Positional parameters are multiplied by 10^4. Anisotropic thermal parameters are defined by the form

$$\exp\left[-(h^2\beta_{11}+k^2\beta_{22}+l^2\beta_{33}+2hk\beta_{12}+2hl\beta_{13}+2kl\beta_{23})\right]$$ and are multiplied by 10^4.

The U_i values are the r.m.s. amplitudes of atomic thermal vibration (in Å × 10^2) derived from the principal components of the β_{ij} tensors.

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}	U_1	U_2	U_3
N(1)	1320 (2)	1402 (0)	9084 (4)	41 (3)	17 (1)	30 (1)	0 (1)	35 (5)	0 (3)	17	21	27
	6121 (2)	3141 (2)	2717 (4)	37 (2)	17 (1)	29 (1)	0 (1)	36 (4)	3 (3)	16	20	27
	6294 (2)	1400 (2)	7678 (5)	44 (3)	17 (1)	30 (1)	0 (1)	−30 (4)	−8 (3)	17	20	28
	1148 (2)	3150 (2)	4141 (5)	40 (2)	17 (1)	30 (1)	1 (1)	−31 (4)	−6 (2)	17	20	28
C(2)	1622 (3)	1949 (2)	8297 (5)	51 (3)	16 (1)	26 (1)	3 (2)	21 (5)	5 (3)	19	20	26
	5826 (3)	2616 (2)	3546 (5)	46 (3)	18 (1)	28 (1)	2 (2)	26 (5)	0 (3)	19	21	27
	6592 (3)	1922 (2)	8559 (5)	47 (3)	18 (1)	29 (1)	1 (1)	−18 (5)	−6 (3)	19	21	26
	0865 (3)	2612 (2)	3290 (5)	50 (3)	18 (1)	27 (1)	3 (1)	−21 (5)	−4 (3)	19	21	26
O(2)	1059 (2)	2388 (2)	8321 (5)	70 (3)	21 (1)	43 (1)	14 (1)	63 (5)	18 (3)	18	24	34
	6368 (2)	2159 (2)	3556 (5)	72 (3)	20 (1)	45 (1)	14 (1)	63 (5)	20 (3)	18	24	35
	6035 (2)	2370 (2)	8606 (5)	65 (2)	21 (1)	43 (1)	18 (1)	−48 (4)	−21 (3)	16	24	35
	1450 (2)	2173 (2)	3263 (5)	68 (2)	20 (1)	45 (1)	13 (1)	−49 (4)	−21 (3)	18	24	35
N(3)	2607 (2)	1956 (2)	7458 (4)	42 (3)	15 (1)	28 (1)	0 (1)	16 (4)	10 (3)	18	19	26
	4830 (2)	2611 (2)	4408 (4)	43 (3)	12 (1)	28 (1)	3 (1)	28 (4)	08 (3)	17	18	27
	7598 (2)	1922 (2)	9447 (4)	41 (2)	14 (1)	29 (1)	2 (1)	−19 (4)	−12 (2)	17	18	27
	−142 (2)	2589 (2)	2452 (4)	43 (2)	13 (1)	30 (1)	1 (1)	−09 (4)	−10 (2)	17	18	27
C(4)	3270 (2)	1476 (2)	7249 (4)	39 (3)	14 (1)	20 (1)	0 (1)	−7 (4)	0 (3)	18	18	22
	4172 (2)	3093 (2)	4566 (4)	32 (3)	16 (1)	18 (1)	−2 (1)	−7 (4)	0 (3)	16	20	21
	8281 (2)	1457 (2)	9506 (4)	39 (3)	13 (1)	21 (1)	−3 (1)	10 (4)	−2 (2)	17	19	22
	−839 (2)	3058 (2)	2346 (5)	38 (3)	14 (1)	22 (1)	0 (1)	8 (4)	−1 (3)	17	19	23
O(4)	4102 (2)	1538 (2)	6350 (3)	33 (2)	17 (1)	26 (1)	−1 (1)	18 (3)	9 (2)	16	20	25
	3345 (2)	3044 (2)	5476 (3)	33 (2)	17 (1)	26 (1)	1 (1)	6 (3)	9 (2)	16	20	25
	9129 (2)	1507 (2)	10406 (3)	37 (2)	18 (1)	25 (1)	0 (1)	−8 (3)	−12 (2)	17	20	25
	−1693 (2)	2987 (2)	1447 (3)	32 (2)	19 (1)	27 (1)	0 (1)	−14 (3)	−7 (2)	16	21	26
C(5)	2974 (2)	876 (2)	8139 (5)	39 (3)	13 (1)	23 (1)	−1 (1)	−1 (5)	5 (3)	17	18	23
	4477 (2)	3682 (2)	3604 (4)	39 (3)	13 (1)	20 (1)	1 (1)	2 (4)	3 (3)	17	18	22
	7985 (2)	866 (2)	8498 (5)	43 (3)	14 (1)	27 (1)	0 (1)	−7 (4)	−12 (3)	17	19	26
	−568 (2)	3648 (2)	3316 (5)	42 (2)	13 (1)	24 (1)	1 (1)	−10 (4)	−5 (2)	18	18	24
C(6)	1900 (2)	878 (2)	9144 (5)	41 (3)	18 (1)	21 (1)	−6 (1)	−3 (4)	−3 (3)	17	22	23
	5545 (2)	3667 (2)	2589 (5)	49 (3)	15 (1)	23 (1)	−2 (2)	−3 (5)	1 (3)	19	20	23
	6893 (2)	883 (2)	7498 (5)	46 (3)	16 (1)	26 (1)	−2 (1)	−8 (4)	−9 (3)	18	20	25
	541 (2)	3658 (2)	4275 (5)	43 (3)	17 (1)	27 (1)	−4 (1)	1 (5)	−1 (3)	18	21	25
O(6)	1548 (2)	437 (2)	9948 (4)	65 (3)	18 (1)	32 (1)	−6 (1)	39 (4)	12 (3)	18	24	29
	5893 (2)	4098 (2)	1724 (4)	67 (3)	17 (1)	34 (1)	−8 (1)	33 (4)	12 (3)	17	24	29
	6544 (2)	451 (2)	6607 (5)	70 (3)	20 (1)	45 (1)	−3 (1)	−4 (4)	−27 (3)	19	24	34
	885 (2)	4106 (2)	5079 (4)	63 (2)	20 (1)	40 (1)	−6 (1)	−29 (4)	−28 (3)	18	24	32
C(7)	3840 (3)	692 (2)	9659 (6)	55 (4)	25 (1)	31 (1)	0 (2)	−26 (6)	34 (4)	18	22	31
	4531 (3)	4180 (2)	5215 (6)	73 (4)	13 (1)	33 (1)	0 (2)	25 (6)	−14 (3)	17	23	29
	7979 (3)	363 (2)	10037 (7)	83 (4)	15 (1)	44 (2)	−1 (2)	−57 (7)	13 (4)	19	23	34
	−1394 (3)	3766 (2)	4946 (6)	56 (3)	22 (1)	29 (1)	4 (2)	01 (5)	−22 (3)	20	22	28
C(8)	4049 (5)	1157 (3)	11233 (7)	072 (5)	44 (2)	29 (2)	−13 (3)	−24 (8)	3 (5)	22	27	34
	5423 (4)	4093 (3)	6720 (6)	104 (6)	29 (1)	26 (2)	−14 (3)	−1 (8)	−12 (5)	22	26	31
	7121 (5)	406 (3)	11565 (8)	148 (6)	39 (2)	35 (2)	−34 (3)	−19 (9)	37 (5)	22	29	41
	−1560 (3)	3234 (3)	6353 (6)	080 (4)	38 (2)	29 (1)	−7 (2)	26 (6)	−6 (4)	23	27	31
C(9)	2904 (3)	404 (2)	6476 (5)	57 (4)	15 (1)	30 (1)	−2 (6)	32 (2)	−6 (3)	19	20	28
	3607 (3)	3841 (2)	2046 (6)	47 (4)	28 (1)	28 (1)	0 (2)	−11 (6)	28 (4)	19	22	30
	8816 (3)	747 (2)	6892 (6)	45 (3)	29 (1)	37 (1)	4 (2)	6 (5)	−39 (4)	18	22	33
	−625 (3)	4149 (2)	1766 (7)	69 (3)	16 (1)	38 (1)	−7 (2)	−42 (6)	14 (3)	18	22	32
C(10)	2027 (4)	524 (2)	4946 (6)	100 (5)	28 (2)	23 (1)	−14 (2)	−10 (6)	−8 (4)	21	25	31
	3416 (4)	3351 (3)	525 (6)	78 (5)	48 (2)	26 (1)	−8 (3)	−43 (7)	6 (5)	20	28	34
	8960 (4)	1249 (3)	5435 (7)	87 (5)	48 (2)	29 (2)	−9 (3)	37 (7)	−9 (5)	23	28	35
	180 (4)	4065 (3)	122 (7)	113 (5)	31 (2)	33 (2)	−23 (3)	0 (8)	15 (5)	22	28	34

Table 2 (*cont.*)

(*b*) Hydrogen atoms
Positional parameter are multiplied by 10^3.

	x	y	z	B(Å^2)
H(1)	69 (3)	141 (2)	965 (6)	3·3 (8)
	667 (3)	319 (2)	216 (6)	4·6 (9)
	569 (4)	138 (2)	702 (7)	5·8 (9)
	178 (3)	314 (2)	480 (6)	4·0 (6)
H(3)	284 (3)	229 (2)	703 (6)	4·3 (9)
	461 (3)	227 (2)	514 (7)	5·6 (10)
	773 (3)	233 (2)	1021 (6)	4·4 (7)
	−27 (3)	227 (2)	181 (6)	4·9 (7)
H(71)	361 (4)	30 (2)	1027 (7)	6·6 (10)
	464 (3)	457 (2)	469 (7)	7·2 (10)
	788 (4)	01 (3)	946 (7)	6·3 (10)
	−110 (4)	408 (3)	580 (9)	5·0 (11)
H(72)	452 (4)	58 (2)	890 (7)	4·3 (10)
	378 (3)	421 (2)	576 (7)	7·1 (10)
	877 (4)	41 (3)	1066 (7)	7·4 (10)
	−205 (4)	387 (3)	432 (9)	5·1 (11)
H(81)	353 (4)	130 (3)	1191 (8)	5·5 (12)
	602 (4)	414 (3)	606 (9)	7·2 (14)
	642 (4)	29 (2)	1078 (8)	7·3 (10)
	−83 (4)	310 (3)	669 (8)	5·1 (11)
H(82)	430 (4)	149 (3)	1080 (8)	8·3 (12)
	536 (4)	367 (3)	727 (9)	8·5 (14)
	711 (4)	84 (3)	1210 (7)	7·3 (10)
	−185 (5)	286 (3)	550 (9)	7·3 (11)
H(83)	456 (4)	107 (3)	1234 (8)	7·3 (12)
	533 (5)	443 (3)	769 (9)	5·7 (14)
	728 (4)	12 (3)	1282 (8)	7·3 (10)
	−207 (5)	335 (3)	755 (9)	7·7 (12)
H(91)	283 (3)	−2 (2)	710 (6)	3·7 (8)
	377 (4)	423 (7)	148 (7)	6·7 (10)
	864 (3)	32 (2)	629 (6)	5·6 (8)
	−51 (3)	457 (2)	242 (6)	4·9 (7)
H(92)	364 (3)	43 (2)	596 (5)	5·8 (8)
	296 (4)	396 (2)	277 (7)	7·0 (10)
	946 (3)	70 (2)	751 (6)	4·9 (8)
	−131 (3)	416 (2)	142 (6)	5·2 (7)
H(101)	139 (4)	50 (3)	574 (8)	8·8 (11)
	420 (4)	320 (2)	9 (7)	6·8 (11)
	829 (4)	135 (3)	472 (7)	6·3 (9)
	85 (4)	412 (2)	95 (7)	6·4 (9)
H(102)	215 (4)	96 (3)	441 (8)	4·2 (11)
	313 (4)	300 (3)	129 (7)	5·4 (11)
	919 (4)	156 (2)	609 (7)	5·8 (9)
	19 (4)	365 (2)	−61 (7)	6·4 (9)
H(103)	223 (4)	19 (3)	377 (8)	7·0 (12)
	273 (4)	345 (2)	−29 (7)	9·1 (11)
	951 (4)	121 (2)	427 (7)	7·3 (10)
	3 (4)	445 (2)	−79 (7)	8·9 (10)

plates, particularly if solvent evaporation is rapid. We have shown that these plates are monoclinic, but are twinned on the well developed (010) face, giving pseudo-orthorhombic diffraction patterns. Earlier, these twinned plates were mistakenly reported as orthorhombic (Ghose, Jeffrey, Craven & Warwicker, 1960).

The crystal data have already been reported (Craven, *et al.*, 1969) but they are repeated here. Lattice translations are $a=12{\cdot}585(8)$, $b=22{\cdot}083(10)$, $c=6{\cdot}788(9)$ Å, $\beta=90°55(2)'$. The systematic spectral absence is $0k0$ with k odd, which is consistent with space group $P2_1$ or $P2_1/m$. There are 8 molecules in the cell, giving a calculated crystal density 1·303 g.cm^{-3} in good agreement with the value of 1·296(7) g.cm^{-3} measured by the flotation method. X-ray intensities were measured on a computer-controlled four-circle diffractometer, using Cu $K\alpha$ radiation with nickel filtering.

The crystal was mounted with the φ axis of the diffractometer coinciding with the reciprocal lattice vector (012). This was also approximately the longest dimension of the crystal, which measured $0{\cdot}2\times0{\cdot}3\times0{\cdot}5$ mm. X-ray reflections were scanned in the θ:2θ mode at 2° min^{-1} in 2θ, with 20-second background counts at each scan limit. Intensities were recorded for 2910 non-symmetry-related reflections with $\sin\theta/\lambda\le0{\cdot}59$Å^{-1}. Of these, 172 were considered to be unobservably weak, since their integrated intensities, I, were less than 1·2 $\sigma(I)$, where $\sigma(I)$ was the standard deviation estimated from counting statistics. These reflections were assigned intensities equal to $\sigma(I)$. No corrections were made for X-ray absorption or extinction.

Crystal structure determination

The observed spectral systematic absence, ($0k0$ absent for k odd) which is normal for the monoclinic system, indicates that barbital IV has either space group $P2_1$ with four molecules in the asymmetric unit (later shown to be the case), or $P2_1/m$ with two molecules in the asymmetric unit. Although the diffraction symmetry was found to be monoclinic, similarities were observed between hkl and $\bar{h}kl$ structure amplitudes (Table 1), particularly at small l values, which were consistent with the pseudo-orthorhombic crystal morphology and the almost orthogonal cell. Also, the reflections $hk0$ with h odd were found to be very weak or unobservably weak, indicating a pseudo a glide plane normal to c. However, the combination of the

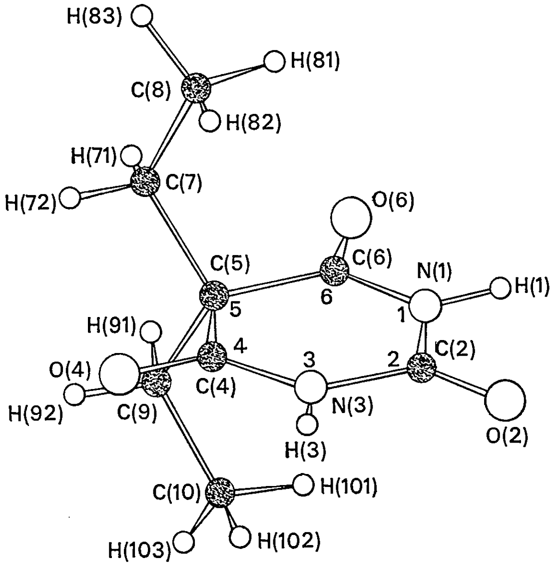

Fig. 1. Molecular stereochemistry and atomic nomenclature for barbital. Atoms of the four independent molecules in barbital IV are all labeled in the same way, with O(4) the oxygen atom that is hydrogen bonded.

2_1 axis along b and a glide plane normal to c implies the presence of a b glide plane normal to a. This glide plane was not indicated by the observed absence or weakness of $0kl$ reflections with k odd, thus confirming the absence of any true glide plane symmetry in the crystal structure.

The distribution of normalized structure factors $E(hkl)$ for barbital IV was consistent with that of a centrosymmetric crystal structure, *i.e.*, with space group $P2_1/m$ rather than $P2_1$ (observed $\langle E\rangle=0{\cdot}793$; $\langle E^2\rangle=0{\cdot}985$; $\langle E^2-1\rangle=0{\cdot}961$; with overall isotropic temperature factor $B=3{\cdot}4$ Å^2; Karle, Dragonette & Brenner, 1965; Wilson, 1942).

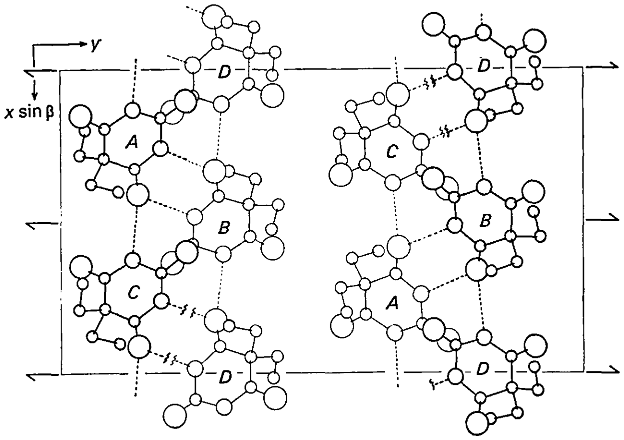

Fig. 2. Molecular packing and hydrogen bonding in barbital IV, viewed down the z axis. One complete unit cell is shown. Hydrogen bonds are dotted.

Application of Patterson and direct methods yielded only a partially correct solution to the phase problem (Vizzini, 1968). The crystal structure was finally determined by trial-and-error methods and by analogy with the crystal structure of vinbarbital (Craven & Cusatis, 1969), which has the same system of hydrogen bonding. Thus, the correct space group for barbital IV was shown to be $P2_1$, with four molecules (A, B, C and D) in the crystal chemical unit.

Fourier refinement based on this model proceeded satisfactorily, followed by a least-squares refinement in the usual block-diagonal approximation. All hydrogen atoms were found in a difference Fourier map. A full-matrix least-squares refinement of all 660 structure parameters was not carried out because of the limitations of available computer programs. Such a procedure would have been preferred, since it takes into account any strong correlations between parameters of different atoms that might arise because of the crystal's pseudosymmetry.

As an alternative, the final least-squares refinement was in five large parameter blocks: (1) Scale factor and 155 atomic positional parameters for the non-hydrogen atoms (y parameter of atom N(1) in molecule A was fixed, to define the crystallographic origin); (2) scale factor and 156 anisotropic temperature factors for the 26 non-hydrogen atoms of molecules A and B; (3) same as (2), but for molecules C and D; (4) the 144 positional parameters for all hydrogen atoms and the 24 isotropic temperature factors for those of molecules A and B; (5) same as (4), but with temperature factors for molecules C and D.

Table 3. *Bond lengths and angles in barbital* IV

The four values of each parameter are from the four different molecules in the cell. Mean values are also given, together with r.m.s. deviations from the mean (in parentheses). The latter are expressed as numbers referred to the least significant digit in the mean.

(*a*) Bond lengths

	A	*B*	*C*	*D*	Mean
N(1)—C(2)	1·375 Å	1·344 Å	1·348 Å	1·366 Å	1·358 (13) Å
C(2)—N(3)	1·373	1·392	1·393	1·381	1·385 (8)
N(3)—C(4)	1·358	1·355	1·339	1·357	1·352 (8)
C(6)—N(1)	1·368	1·370	1·375	1·359	1·368 (6)
C(4)—C(5)	1·505	1·507	1·516	1·498	1·507 (7)
C(5)—C(6)	1·523	1·521	1·523	1·531	1·525 (4)
C(2)—O(2)	1·201	1·216	1·212	1·217	1·212 (6)
C(4)—O(4)	1·228	1·223	1·227	1·237	1·229 (5)
C(6)—O(6)	1·204	1·204	1·208	1·206	1·205 (2)
C(5)—C(7)	1·544	1·551	1·524	1·552	1·543 (11)
C(5)—C(9)	1·537	1·549	1·544	1·526	1·539 (7)
C(7)—C(8)	1·502	1·518	1·511	1·529	1·515 (10)
C(9)—C(10)	1·526	1·512	1·497	1·530	1·516 (13)
N(1)—H(1)	0·88	0·80	0·88	0·90	0·87 (4)
N(3)—H(3)	0·84	0·94	1·05	0·84	0·92 (7)
C(7)—H(71)	1·01	0·94	0·89	0·97	0·95 (5)
C(7)—H(72)	1·04	1·02	0·97	0·96	1·00 (3)
C(8)—H(81)	0·87	0·88	1·06	0·99	0·95 (8)
C(8)—H(82)	0·86	1·00	1·03	1·07	0·99 (8)
C(8)—H(83)	1·00	0·99	1·08	1·08	1·04 (4)
C(9)—H(91)	1·03	0·97	1·05	1·03	1·02 (3)
C(9)—H(92)	1·00	0·99	0·91	0·89	0·95 (5)
C(10)—H(101)	0·97	1·09	0·99	1·02	1·02 (5)
C(10)—H(102)	1·05	1·01	0·87	1·03	0·99 (7)
C(10)—H(103)	1·13	1·04	1·06	1·07	1·08 (4)

Table 3 (*cont.*)

(*b*) Bond angles

C(2)—N(1)—C(6)	127·1°	127·5°	126·9°	127·1°	127·2 (2)°
C(2)—N(1)—H(1)	114	124	120	114	118 (4)
C(6)—N(1)—H(1)	119	109	113	118	115 (3)
N(1)—C(2)—N(3)	115·4	116·0	115·8	115·9	115·8 (2)
N(1)—C(2)—O(2)	122·5	124·0	123·5	123·0	123·3 (6)
N(3)—C(2)—O(2)	122·1	119·9	120·7	121·1	121·0 (8)
C(2)—N(3)—C(4)	126·4	125·6	126·3	125·6	126·0 (4)
C(2)—N(3)—H(3)	119	120	110	115	116 (3)
C(4)—N(3)—H(3)	115	113	123	119	118 (4)
N(3)—C(4)—C(5)	119·2	119·0	119·6	119·9	119·4 (3)
N(3)—C(4)—O(4)	119·6	119·7	119·9	119·1	119·7 (3)
C(5)—C(4)—O(4)	121·1	121·3	120·5	121·0	121·0 (3)
C(4)—C(5)—C(6)	113·9	114·2	113·1	113·5	113·7 (4)
C(4)—C(5)—C(7)	108·9	108·3	108·8	108·0	108·5 (4)
C(4)—C(5)—C(9)	108·3	108·0	107·5	108·7	108·1 (3)
C(6)—C(5)—C(7)	108·9	107·8	108·0	108·1	108·2 (4)
C(6)—C(5)—C(9)	106·8	108·4	107·8	108·4	107·9 (7)
C(7)—C(5)—C(9)	110·1	110·1	111·8	110·2	110·6 (7)
C(5)—C(6)—N(1)	117·7	117·4	118·2	117·9	117·8 (3)
C(5)—C(6)—O(6)	122·4	122·3	121·4	121·5	121·9 (4)
N(1)—C(6)—O(6)	119·8	120·3	120·4	120·6	120·3 (3)
C(5)—C(7)—C(8)	114·1	114·1	115·9	114·6	114·7 (7)
C(5)—C(7)—H(71)	107	113	110	107	109 (3)
C(5)—C(7)—H(72)	108	106	102	108	106 (3)
H(71)—C(7)—H(72)	104	103	113	114	109 (5)
C(7)—C(8)—H(81)	120	106	104	104	109 (7)
C(7)—C(8)—H(82)	114	108	108	108	110 (3)
C(7)—C(8)—H(83)	120	105	112	112	112 (5)
H(81)—C(8)—H(82)	99	111	113	101	106 (6)
H(81)—C(8)—H(83)	99	111	113	118	108 (7)
H(82)—C(8)—H(83)	101	115	106	113	109 (6)
C(5)—C(9)—C(10)	114·5	114·0	115·6	113·0	114·3 (9)
C(5)—C(9)—H(91)	108	108	106	110	108 (2)
C(5)—C(9)—H(92)	100	107	107	104	105 (3)
H(91)—C(9)—H(92)	106	98	105	102	103 (3)
C(9)—C(10)-H(101)	102	106	112	98	105 (5)
C(9)—C(10)-H(102)	107	105	107	118	109 (5)
C(9)—C(10)-H(103)	102	109	121	102	109 (8)
H(101)-C(10)-H(102)	112	104	110	111	109 (3)
H(101)-C(10)-H(103)	124	132	102	111	117 (12)
H(102)-C(10)-H(103)	109	99	103	116	107 (6)

The parameter variance-covariance matrix for block (1) showed that all *y* parameters were significantly correlated, as to be expected in an equi-atom structure with a polar *b* axis (Templeton, 1960). Correlation coefficients were about 0·7 for corresponding atoms in pseudosymmetrically related molecules; otherwise, they were about 0·4. These factors did not prevent a satisfactory convergence of the refinement. The refinements for blocks (2) and (3) were terminated before convergence because of the excessive consumption of computer time. In the final cycles, parameter changes as large as $4\sigma(\beta_{ij})$ occurred. Although they may have less than their usual physical significance, the derived root-mean-square amplitudes of thermal vibration (Table 2) are similar to those found in related barbiturate crystal structures.

Final R values* were 0·046 for all reflections and 0·044 for observed reflections only. Corresponding weighted R values were 0·060 and 0·058. The weighting scheme was $w=1/\sigma^2(F)$ with $\sigma^2(F)=0{\cdot}3+0{\cdot}002\ F^2$. The C, N, and O atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1962). The H-atom scattering factors were those of Stewart, Davidson & Simpson (1965). Observed and calculated structure amplitudes are listed in Table 1. In the course of the refinement, nine strong low-order reflections were given zero weight because the calculated amplitudes were much greater than observed values. These reflections are marked by (*) in Table 1. Atomic parameters with their estimated standard deviations are listed in Table 2.

Discussion

In the crystal structure of barbital IV (Fig. 2) four molecules exist in very similar environments,* so that

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* $R=(\sum_{hkl}|(|F_{\rm obs}|-|F_{\rm calc}|)|/\sum_{hkl}F_{\rm obs}|$

* Atoms in each barbital molecule are labeled as in Fig. 1. In the isolated molecule of this and other barbiturates with twofold ring symmetry, the sense for numbering ring atoms is undefined. In barbiturate crystal structures it is proposed, henceforth, that the ring should be numbered so that the carbonyl group C(4)=O(4) is hydrogen bonded.

the corresponding bond lengths and angles (Table 3) should be the same within experimental error. However, this is not true for all bond lengths and angles in terms of e.s.d.'s derived from the inverse matrix of the least-squares procedure. The latter are about 0·005 Å for C–O, C–N, and C–C(5) bond lengths, 0·008 Å for other C–C bond lengths, 0·05 Å for N–H and C–H bond lengths, and 0·2° for ring bond angles. The pair of corresponding bond lengths that differs the greatest (4·2σ) is C(2)–N(1) in molecules *A* and *B* (1·375 and 1·344 Å).* The r.m.s. deviation from the mean of the four C(2)–N(1) bond lengths (0·013 Å) is three times the corresponding least-squares e.s.d. However, the overall r.m.s. deviation of C–O, C–N, and ring C–C bond lengths from their nine respective mean values (0·007 Å) is not much in excess of the least-squares e.s.d. (0·005 Å). Both values are underestimates because of the neglect of systematic errors.

Bond lengths and angles in barbital IV are similar to those found in the crystal structures of barbital I and II (Craven *et al.*, 1969), and other barbituric acids with alkyl or alkenyl substituents at C(5), such as amobarbital I and II (Craven & Vizzini, 1969), γ-methylamobarbital (Gartland & Craven, 1971), vinbarbital (Craven & Cusatis, 1969), and in the 2:1 complex of barbital and caffeine (Craven & Gartland, unpublished). In these crystal structures (excluding barbital IV), there are eight distinct molecules in which the carbonyl-oxygen atom O(4) is hydrogen bonded and oxygen atom O(6) is not. The twofold ring symmetry is very nearly preserved in these molecules, but there are small C=O and C–N bond length differences (about 0·01 Å) between corresponding bonds in the two halves of the ring. The hydrogen-bonded C(4)–O(4) carbonyl bond length is a little longer than that of C(6)–O(6), the adjacent C(4)–N(3) length is shorter than C(6)–N(1), and N(3)–C(2) is longer than N(1)–C(2). The same pattern exists in barbital IV, except that bond lengths N(3)–C(2) and N(1)–C(2) in molecule *A* differ slightly in the reverse sense (0·002 Å). In each of these molecules, including those in barbital IV, individual bond-length differences are insignificant, or only possibly significant in terms of their e.s.d.'s. However, the recurrence of such features suggests that they may be real and represent the effects of hydrogen bonding on the otherwise symmetrical conjugated system O(4)–C(4)–N(3)–C(2)–N(1)–C(6)–O(6).

The four molecules in barbital IV have conformations similar to those found in other crystal structures containing barbital. Ring atoms are almost coplanar, and the ethyl-carbon atoms and C(5) form a chain extending normal to the ring. The slightly skew form of the rings is shown in Fig. 3. The C(8)–C(7)–C(5)–C(9)–C(10) chains are slightly twisted into 's' shapes in the view down the molecular C(5)···C(2) axes. Torsion angles C(8)–C(7) → C(5)–C(9) are +173·9, −175·1, −174·3, and +168·6° for molecules *A*, *B*, *C*, *D* respectively.* Torsion angles C(10)–C(9) → C(5)–C(7) are +176·7, −174·1, −173·9, and +179·3°. Thus, there is approximate twofold symmetry about the molecular axes C(5)···C(2). It is interesting to note that if the hydrogen-bonded carbonyl C(4)–O(4) is considered to be different from C(6)–O(6), then molecules *A* and *D* have very similar conformations which, in turn, are almost enantiomorphous to those of molecules *B* and *C*. This pseudoracemic relationship is consistent with the pseudosymmetry elements in the crystal structure.

The mode of intermolecular NH···O=C hydrogen bonding in barbital IV (Fig. 2 & Table 4) is the same as in 5-ethyl-5-(1′-methylbutenyl)-barbituric acid or vinbarbital (Craven & Cusatis, 1969) and 5-ethyl-5-[1′-cyclohepten-(1′)-yl]-barbituric acid or heptabarbital (Bideau, Leroy & Housty, 1969). One carbonyl group, C(4)–O(4), accepts both hydrogen bonds, giving rise to a sandwich-like sheet of hydrogen-bonded mole-

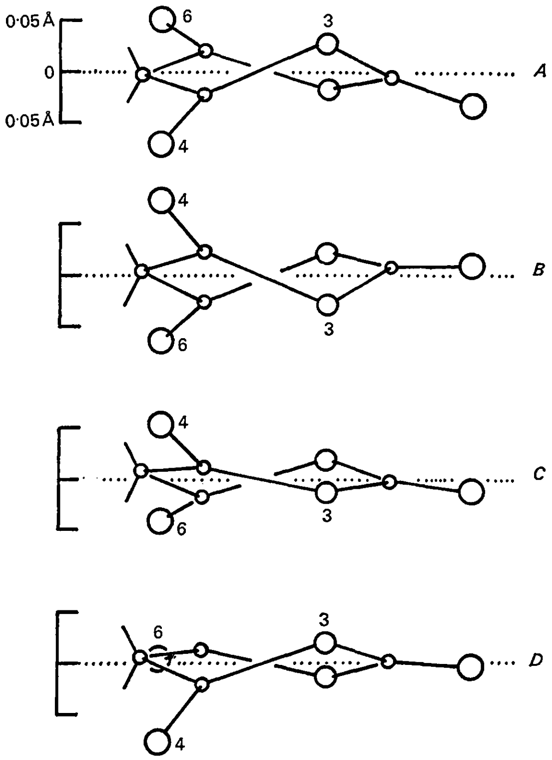

Fig. 3. Ring conformations of the four independent molecules. Scale in the vertical direction is greatly exaggerated, as shown. Dotted lines represent the trace of the best least-squares planes through the six pyrimidine ring atoms of each molecule. Hydrogen-bonded carbonyl groups C(4)–O(4) project towards the viewer.

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* According to an expression developed by Gartland (1970), which takes into account all correlations among the 12 positional parameters, the e.s.d. in each of these bond lengths is 0·0045 Å and the e.s.d. in their difference (0·031 Å) is 0·0073 Å.

* A positive torsion angle is defined as a clockwise twist of the back bond with respect to the front bond, when the four atoms are viewed down the central bond.

cules. The polar ring portions of the barbiturate molecules, except for the C(6)–O(6) carbonyl group, are inside the sandwich, while the nonpolar C(5) substituents and atom O(6) form the outside. In these three crystal structures, the sheet repeat distances are crystal lattice translations that are very similar, since they are largely determined by the hydrogen bonding of the common moiety (12·59 × 6·79 Å in barbital IV; 12·54 × 6·82 Å in vinbarbital, and 12·44 × 6·84 Å in heptabarbital).

Table 4. *Intermolecular distances and angles*

(*a*) Hydrogen bonds

The range of each of the four pseudosymmetrically related parameters in barbital IV is listed together with the corresponding values from vinbarbital (Craven & Cusatis, 1969).

	Barbital IV	Vinbarbital
$O(4)\cdots N(3)$	2·852–2·911 Å	2·866 Å
$O(4)\cdots N(1)$	2·904–2·921	2·924
$C(4)—O(4)\cdots N(3)$	125·3–127·0°	126·2°
$C(4)—O(4)\cdots N(1)$	130·4–131·1	130·4
$O(4)\cdots H(3)—N(3)$	165 –174	175
$O(4)\cdots H(1)—N(1)$	155 –168	166
$H(1)\cdots O(4)\cdots H(3)$	82 – 85	86

(*b*) Interatomic distances between hydrogen bonded sheets

The list contains the shortest distances from each oxygen atom O(6) to an ethyl-carbon atom, and all ethyl $H\cdots H$ distances less than 2·7 Å.

$O(6)A\cdots C(9)D^{*}$	3·28 Å	$H(101)A\cdots H(91)D^{*}$	2·65 Å
$O(6)B\cdots C(9)A^{\dagger}$	3·47	$H(72)B\cdots H(83)C^{\S}$	2·60
$O(6)C\cdots C(7)B^{\ddagger}$	3·34	$H(71)C\cdots H(81)D^{\dagger}$	2·54
$O(6)D\cdots C(9)C^{\dagger}$	3·87	$H(72)C\cdots H(83)D^{\dagger}$	2·66

Symmetry operations:

$*$: $-x, -\frac{1}{2}+y, 1-z$
$\dagger$: $1-x, \frac{1}{2}+y, 1-z$
$\ddagger$: $1-x, -\frac{1}{2}+y, 1-z$
$\S$: $1-x, -\frac{1}{2}+y, 2-z$

The sandwich structures stack together, so that only weak van der Waals interactions exist between them. In vinbarbital and heptabarbital, adjacent sheets are related by simple lattice translations, so that the four molecules in the cell are all related by the space group symmetry $P2_1/c$. In barbital IV, adjacent sheets are related by the crystallographic 2_1 axis parallel to **b**. Molecules within the same sheet are related by pseudo $2_1/a$ symmetry. For the sheet extending from $y=0$ to $\frac{1}{2}$ (Fig. 2), there are: pseudo a glide planes at approximately $z=0·34$ and 0·84; pseudo 2_1 axes parallel to z at $x=0·12$, $y=0·23$ and $x=0·62$; $y=0·23$ and pseudocenters of symmetry at (0·37, 0·23, 0·59), (0·87, 0·23, 0·59), *etc.*

The phase equilibria of binary barbiturate systems involving barbital, vinbarbital, and heptabarbital with each other are not among the many studied by Brandstätter-Kuhnert and her co-workers. However, Brandstätter-Kuhnert & Aepkers (1963) report that barbital IV forms solid solutions in all proportions with 5-ethyl-5-allyl-barbituric acid, polymorph III; 5-ethyl-5-sec-butyl-barbituric acid, polymorph I (m.p. min. of 153 °C); 5-ethyl-5-isopropyl-barbituric acid, polymorph I; and 5-allyl-5-isopropyl-barbituric acid, polymorph III. They conclude that the crystal structures of these end members are isomorphous, which presumably means that they have the same hydrogen-bonded sheet framework as barbital IV. The geometry of this framework places steric restrictions on the C(5) substituents, which are partially enclosed by other molecules from the same sheet. A substituent with an extended chain of three or more carbon atoms cannot be accommodated. Note that all crystal structures reported to be isomorphous with barbital IV, as well as vinbarbital and heptabarbital, are those of barbiturates with C(5) substituents which are either ethyl groups, or (if larger than ethyl) groups that can adopt a conformation satisfying the steric restrictions imposed by the hydrogen-bonded framework.

Most of the computer programs used in this research were written or modified by Professor R. Shiono. The work was supported by Grant No. NS-02763 of the U.S. Public Health Service, National Institutes of Health.

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