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The Crystal Structure of Sodium 5,5-Diethylbarbiturate (Sodium Barbital)

BY B. BERKING AND B. M. CRAVEN

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

The crystal structure of sodium 5,5-diethylbarbiturate $NaC_8N_2O_3H_{11}$ (sodium barbital) has been determined from X-ray diffraction data measured on an automatic diffractometer. $R = 0.025$. The crystal data are: $P2_12_12_1$, $a = 6.724$ (1), $b = 11.950$ (2), $c = 12.129$ (2) Å, $Z = 4$, $D_m = 1.408$ g.cm^{-3}. The conformation of the barbital ion is similar to that of the barbital molecule. Deprotonization of the pyrimidine ring at N(3) decreases the internal bond angle at N(3) by 7° and increases those at the neighbouring atoms C(2) and C(4) by 5°. The greater part of the formal negative charge seems to be equally distributed between the two oxygen atoms O(2) and O(4). The molecules are hydrogen bonded (NH$\cdots$O = 2.84 Å) to form ribbons along the a axis. The sodium atom is tetrahedrally coordinated by barbital oxygen atoms, with tetrahedra sharing corners to form columns parallel to a.

Introduction

We report the crystal structure determination of sodium 5,5-diethylbarbiturate (sodium barbital, Fig. 1) as part of a program for studying and comparing the tautomeric form, stereochemistry and intermolecular interactions of simple barbituric acids and their salts. A series of crystal structures have been determined, including barbituric acid (Bolton, 1963), its dihydrate (Jeffrey, Ghose & Warwicker, 1960) and ammonium salt (Craven, 1963); 5-ethylbarbituric acid (Gatehouse & Craven, 1971) and the $\frac{2}{3}$ hydrate of its potassium salt (Gartland, Craven & Gatehouse, 1971); and 5,5-diethylbarbituric acid or barbital (Craven, Vizzini & Rodrigues, 1969) and its sodium salt presently reported).

Barbituric acid and 5-ethylbarbituric acid have at least one hydrogen atom at C(5), whereas barbital has none. It is of interest to note that the crystal structures of salts of barbituric acid and 5-ethylbarbituric acid show the formation of carbanions, *i.e.* proton loss is from C(5), whereas in the case of barbital, proton loss is necessarily from an imine nitrogen atom. Barbital is a weaker acid than barbituric acid, as shown by the acid dissociation constants ($pK_a = 7.86$, 3.90 respectively; Doornbos & de Zeeuw, 1969). The pK_a value for 5-ethylbarbituric acid has not been reported.

The crystal structure determination of potassium barbital, based on photographic X-ray intensity data, was reported by Berthou, Rérat & Rérat (1965). The sodium salt was described as isomorphous (Berthou, Cavelier, Marek, Rérat & Rérat, 1962). In order to

obtain more accurate geometry for the barbital ion and to permit a better comparison with that of the parent acid, we have determined the crystal structure of the sodium salt using diffractometer intensity data.

Experimental

Transparent, single crystals of sodium barbital were obtained from aqueous solution by slow evaporation at room temperature. The crystals were stable in the X-ray beam. The crystal data are:

$a = 6{\cdot}724\ (1)$ Å
$b = 11{\cdot}950\ (2)$
$c = 12{\cdot}129\ (2)$
M.W. 206·18
Space group $P2_12_12_1$
$D_m = 1{\cdot}408$ g.cm^{-3}
$D_x = 1{\cdot}404$ g.cm^{-3}
Crystal habit, prisms along {100}
Absorption coefficient, 13·1 cm^{-1} (for Cu $K\alpha$)

The lattice parameters and X-ray intensities were obtained on an automatic diffractometer using Ni-filtered Cu $K\alpha$ radiation. A crystal with dimensions $0{\cdot}5 \times 0{\cdot}2 \times 0{\cdot}15$ mm^3 was mounted with **a** along the diffractometer φ axis. Intensities for 987 reflections were measured by scanning in the θ–2θ mode up to $2\theta = 130°$. Of these, 65 reflections were considered to be unobserved, because their net intensities did not exceed twice the estimated standard deviation from counting statistics. Absorption corrections were not applied.

Structure determination and refinement

Berthou *et al.* (1962) reported that the crystal structures of sodium and potassium barbital are isomorphous and listed approximate atomic coordinates for the sodium salt which they had refined to give R values of 0·27 and 0·25 for the $hk0$ and $h0l$ zones respectively.*

Table 1. $|F_o|$ *and* $|F_c|$ *multiplied by* 10. *The reflections* 011, 002, 021, 022, 111, 032, 033 *and* 211 *are omitted*

H= 0 K= 0		
4	240	231
6	283	285
8	9	6
10	434	456
12	148	145
14	94	98
H= 0 K= 1		
2	18	13
3	33	30
4	79	82
5	317	320
6	171	172
7	227	235
8	94	91
9	46	46
10	9	4
11	20	17
12	26	23
13	33	34
14	7	7
H= 0 K= 2		
0	422	441
3	525	561
4	105	104
5	67	65
6	148	144
7	28	28
8	186	189
9	51	54
10	77	72
11	139	139
12	180	183
13	27	25
14	8	8
H= 0 K= 3		
1	443	465
4	111	120
5	285	283
6	157	154
7	7	4
8	36	39
9	26	23
10	165	163
11	32	33
12	9	1
13	84	85
H= 0 K= 4		
0	541	571
1	335	345
2	111	110
3	645	673
4	155	154
5	36	37
6	105	108
7	114	111
8	106	103
9	217	225
10	31	31
11	91	95
12	18	14
13	23	23
H= 0 K= 5		
1	383	394
2	246	251
3	416	422
4	363	369
5	121	124
6	23	24
7	158	159
8	86	87
9	100	104
10	57	59
11	45	47
12	31	29
13	8	9
H= 0 K= 6		
0	139	138
1	29	27
2	428	438
3	249	252
4	244	260
5	260	263
6	9	4
7	156	159
8	172	169
9	211	218
10	29	23
11	9	9
12	8	7
H= 0 K= 7		
1	287	291
2	158	155
3	403	418
4	249	251
5	139	144
6	273	275
7	196	193
8	87	81
9	58	58
10	66	68
11	20	20
12	8	6
H= 0 K= 8		
0	212	210
1	84	86
2	98	99
3	42	42
4	217	222
5	106	107
6	98	100
7	120	129
8	86	88
9	28	26
10	27	25
11	8	11
H= 0 K= 9		
1	21	20
2	118	123
3	66	64
4	24	21
5	370	380
6	222	224
7	176	177
8	124	128
9	71	72
10	24	22
H= 0 K= 10		
0	10	7
1	50	49
2	45	45
3	37	38
4	10	6
5	111	110
6	57	54
7	68	71
8	99	99
9	20	16
10	91	89
H= 0 K= 11		
1	120	125
2	9	5
3	9	12
4	23	25
5	136	138
6	78	79
7	43	45
8	53	54
H= 0 K= 12		
0	141	142
1	19	20
2	9	5
3	9	6
4	191	194
5	31	30
6	79	80
7	47	46
H= 0 K= 13		
1	52	53
2	28	31
3	146	148
4	47	45
5	46	47
H= 0 K= 14		
0	40	42
1	7	7
H= 1 K= 0		
1	254	255
2	296	302
3	341	333
4	221	223
5	33	27
6	283	268
7	308	309
8	140	138
9	82	76
10	80	82
11	31	33
12	63	64
13	229	228
14	61	59
H= 1 K= 1		
1	171	166
2	427	443
3	395	401
4	263	260
5	351	358
6	153	153
7	281	286
8	137	141
9	9	12
10	170	175
11	116	116
12	172	175
13	30	33
14	79	79
H= 1 K= 2		
0	13	18
1	355	375
2	216	229
3	276	284
4	393	397
5	68	66
6	405	407
7	105	106
8	147	144
9	118	119
10	118	120
11	141	141
12	143	143
13	115	115
H= 1 K= 3		
0	182	179
1	141	136
2	265	280
3	432	460
4	443	443
5	398	405
6	288	288
7	164	166
8	118	116
9	121	124
10	202	204
11	167	164
12	114	113
13	76	74
H= 1 K= 4		
0	171	154
1	381	386
2	225	221
3	193	191
4	518	527
5	139	142
6	161	164
7	137	130
8	169	172
9	132	132
10	167	165
11	146	142
12	32	33
13	53	52
H= 1 K= 5		
0	249	258
1	271	274
2	194	189
3	34	34
4	84	74
5	108	[illegible]
6	53	50
7	156	156
8	41	40
9	260	262
10	128	131
11	28	23
12	24	20
13	8	11
H= 1 K= 6		
0	92	93
1	377	376
2	134	131
3	202	199
4	182	182
5	65	68
6	144	148
7	79	79
8	203	205
9	204	205
10	90	88
11	24	25
12	41	45
H= 1 K= 7		
0	34	31
1	59	62
2	185	183
3	157	157
4	88	91
5	161	164
6	70	70
7	117	118
8	75	77
9	113	112
10	86	89
11	28	25
12	89	85
H= 1 K= 8		
0	21	17
1	78	75
2	183	184
3	58	55
4	118	118
5	306	316
6	70	66
7	89	90
8	188	188
9	44	46
10	26	24
11	79	81
H= 1 K= 9		
0	214	217
1	147	149
2	170	173
3	97	96
4	100	100
5	35	35
6	52	50
7	231	230
8	69	70
9	77	78
10	72	68
H= 1 K= 10		
0	141	137
1	130	129
2	120	117
3	93	98
4	42	42
5	70	69
6	178	179
7	59	60
8	96	99
9	38	34
H= 1 K= 11		
0	27	23
1	119	120
2	114	115
3	10	11
4	45	40
5	143	147
6	89	88
7	45	44
8	91	88
H= 1 K= 12		
0	44	42
1	111	114
2	25	22
3	29	26
4	63	63
5	91	93
6	52	51
7	23	22
H= 1 K= 13		
0	34	32
1	32	31
2	63	63
3	61	63
4	102	99
5	25	26
H= 2 K= 0		
0	249	244
1	248	247
2	72	75
3	124	126
4	146	143
5	22	16
6	321	312
7	505	503
8	59	61
9	169	171
10	77	78
11	80	83
12	40	39
13	8	8
H= 2 K= 1		
0	263	270
2	120	118
3	48	50
4	128	122
5	170	166
6	343	335
7	31	30
8	236	234
9	135	136
10	120	123
11	68	66
12	54	51
13	71	74
H= 2 K= 2		
0	319	313
1	212	211
2	289	294
3	267	266
4	265	256
5	329	326
6	225	213
7	235	231
8	67	62
9	103	101
10	111	109
11	43	43
12	81	84
13	18	18
H= 2 K= 3		
0	52	53
1	114	111
2	154	159
3	273	262
4	228	221
5	197	184
6	112	112
7	50	48
8	75	74
9	151	147
10	90	90
11	98	102
12	19	14
13	47	46
H= 2 K= 4		
0	29	27
1	153	155
2	120	120
3	108	103
4	408	406
5	74	69
6	172	172
7	62	61
8	36	32
9	132	126
10	130	131
11	71	73
12	80	81
13	27	23
H= 2 K= 5		
0	164	167
1	181	173
2	127	124
3	314	309
4	292	293
5	113	120
6	123	122
7	62	60
8	122	118
9	62	61
10	139	143
11	116	115
12	7	7
H= 2 K= 6		
0	68	71
1	110	106
2	371	374
3	170	172
4	90	90
5	192	189
6	81	78
7	193	189
8	97	91
9	150	151
10	72	75
11	31	33
12	34	31
H= 2 K= 7		
0	106	109
1	240	234
2	177	176
3	96	93
4	100	96
5	135	137
6	150	147
7	31	32
8	196	203
9	82	80
10	85	84
11	70	65
H= 2 K= 8		
0	132	131
1	46	49
2	75	74
3	119	117
4	121	119
5	149	147
6	93	94
7	153	159
8	41	45
9	21	21
10	25	23
11	41	41
H= 2 K= 9		
0	106	101
1	122	118
2	80	77
3	21	16
4	88	90
5	30	28
6	130	133
7	10	5
8	24	19
9	37	35
10	8	5
H= 2 K= 10		
0	10	12
1	93	95
2	77	76
3	26	23
4	10	15
5	56	54
6	38	38
7	65	64
8	43	42
9	22	19
H= 2 K= 11		
0	10	11
1	64	63
2	65	65
3	56	58
4	62	63
5	98	99
6	75	72
7	8	14
8	56	57
H= 2 K= 12		
0	48	50
1	9	13
2	57	57
3	81	84
4	61	63
5	50	47
6	8	13
H= 2 K= 13		
0	28	24
1	57	56
2	25	25
3	54	55
4	101	101
H= 3 K= 0		
1	358	371
2	86	75
3	162	158
4	32	26
5	44	46
6	317	310
7	34	34
8	25	18
9	69	71
10	9	11
11	126	129
12	8	8
13	100	105
H= 3 K= 1		
0	671	700
1	325	324
2	49	49
3	300	292
4	35	34
5	156	145
6	73	72
7	35	32
8	76	74
9	37	34
10	87	91
11	75	77
12	42	43
13	46	44
H= 3 K= 2		
0	237	225
1	462	477
2	145	139
3	138	142
4	129	129
5	123	121
6	96	96
7	125	128
8	95	91
9	91	93
10	40	35
11	88	92
12	32	32
13	63	65
H= 3 K= 3		
0	377	372
1	146	139
2	400	401
3	247	248
4	206	209
5	73	75
6	72	73
7	55	56
8	72	75
9	93	94
10	96	97
11	74	77
12	111	110
H= 3 K= 4		
0	134	135
1	260	259
2	220	220
3	369	376
4	71	70
5	92	91
6	109	109
7	92	92
8	10	12
9	19	17
10	105	106
11	103	103
12	34	35
H= 3 K= 5		
0	235	233
1	66	63
2	226	220
3	277	275
4	79	81
5	45	45
6	50	48
7	23	24
8	51	52
9	127	130
10	69	64
11	76	78
12	39	39
H= 3 K= 6		
0	40	35
1	63	59
2	121	120
3	95	97
4	218	216
5	53	55
6	30	31
7	40	38
8	98	99
9	9	3
10	33	36
11	40	39
H= 3 K= 7		
0	9	9
1	8	11
2	112	111
3	53	52
4	65	61
5	144	145
6	113	112
7	107	112
8	45	44
9	67	71
10	21	20
11	8	4
H= 3 K= 8		
0	45	46
1	212	213
2	73	76
3	90	93
4	28	25
5	38	40
6	132	133
7	95	95
8	76	78
9	60	59
10	8	7
H= 3 K= 9		
0	260	260
1	55	51
2	69	72
3	68	69
4	148	149
5	81	83
6	132	130
7	98	103
8	48	50
9	33	32
H= 3 K= 10		
0	69	73
1	142	140
2	10	17
3	106	102
4	34	32
5	108	110
6	52	50
7	8	10
8	38	36
H= 3 K= 11		
0	30	31
1	48	46
2	115	113
3	38	33
4	91	92
5	28	28
6	32	35
7	26	26
H= 3 K= 12		
0	25	24
1	47	44
2	69	69
3	85	87
4	28	26
5	33	33
H= 3 K= 13		
0	8	14
H= 4 K= 0		
0	255	241
1	149	152
2	230	220
3	119	113
4	227	213
5	184	184
6	45	42
7	296	301
8	50	49
9	42	41
10	33	34
11	76	75
12	97	100
H= 4 K= 1		
0	58	53
1	118	118
2	170	172
3	195	188
4	138	134
5	70	70
6	264	268
7	174	175
8	161	156
9	109	110
10	66	67
11	90	92
12	71	71
H= 4 K= 2		
0	218	203
1	232	230
2	138	133
3	86	87
4	106	106
5	272	278
6	96	90
7	58	57
8	132	131
9	136	136
10	57	60
11	93	94
12	81	83
H= 4 K= 3		
0	154	153
1	129	130
2	104	101
3	85	81
4	259	262
5	130	130
6	22	21
7	119	119
8	47	47
9	88	88
10	105	105
11	69	69
H= 4 K= 4		
0	54	55
1	135	134
2	59	57
3	51	44
4	162	161
5	260	262
6	71	66
7	118	116
8	108	110
9	80	83
10	148	152
11	42	42
H= 4 K= 5		
0	71	71
1	95	92
2	264	265
3	201	203
4	232	237
5	57	56
6	90	89
7	34	29
8	84	88
9	103	101
10	67	66
11	31	30
H= 4 K= 6		
0	29	29
1	110	108
2	174	176
3	180	183
4	109	108
5	105	106
6	57	58
7	109	109
8	21	18
9	165	165
10	61	58
H= 4 K= 7		
0	56	58
1	147	146
2	118	115
3	72	71
4	114	115
5	70	67
6	187	192
7	20	20
8	143	142
9	25	22
10	65	65
H= 4 K= 8		
0	180	179
1	94	96
2	147	146
3	56	51
4	124	124
5	70	70
6	44	46
7	91	90
8	48	45
9	54	51
H= 4 K= 9		
0	26	21
1	107	108
2	53	53
3	9	6
4	31	32
5	81	80
6	47	46
7	38	39
8	22	19
H= 4 K= 10		
0	10	4
1	99	98
2	36	27
3	40	43
4	46	47
5	9	10
6	8	5
H= 4 K= 11		
0	27	28
1	116	115
2	84	84
3	32	33
4	53	51
5	51	52
H= 4 K= 12		
0	93	90
1	39	41
H= 5 K= 0		
1	157	151
2	24	24
3	63	60
4	146	148
5	83	82
6	333	335
7	121	123
8	68	65
9	149	150
10	24	20
11	66	68
H= 5 K= 1		
0	217	215
1	70	68
2	27	26
3	107	111
4	27	25
5	174	179
6	143	142
7	198	196
8	10	12
9	95	94
10	120	121
H= 5 K= 2		
0	9	13
1	169	167
2	97	98
3	49	47
4	170	170
5	276	283
6	185	183
7	49	48
8	240	246
9	26	26
10	30	30
H= 5 K= 3		
0	103	109
1	87	83
2	48	50
3	72	72
4	287	291
5	94	95
6	180	178
7	173	171
8	77	76
9	149	150
10	109	110
H= 5 K= 4		
0	233	234
1	57	55
2	88	94
3	320	327
4	94	96
5	125	124
6	124	126
7	137	137
8	99	95
9	117	116
10	136	134
H= 5 K= 5		
0	128	128
1	49	48
2	254	256
3	65	62
4	119	119
5	199	199
6	46	43
7	75	78
8	163	162
9	37	38
H= 5 K= 6		
0	59	59
1	165	165
2	34	30
3	136	136
4	64	61
5	77	79
6	58	56
7	26	30
8	35	33
9	67	67
H= 5 K= 7		
0	185	181
1	108	107
2	179	180
3	93	92
4	105	108
5	49	49
6	76	75
7	49	51
8	71	71
H= 5 K= 8		
0	138	138
1	139	138
2	62	60
3	74	72
4	10	17
5	23	23
6	80	80
7	51	50
H= 5 K= 9		
0	145	150
1	133	134
2	96	100
3	62	60
4	49	48
5	72	78
6	49	48
H= 5 K= 10		
0	100	98
1	68	70
2	52	52
3	41	43
4	109	109
H= 6 K= 0		
0	88	89
1	173	174
2	210	204
3	11	15
4	143	144
5	143	143
6	10	15
7	145	146
8	91	91
9	9	12
H= 6 K= 1		
0	167	172
1	129	137
2	73	72
3	174	175
4	129	127
5	26	25
6	29	30
7	68	69
8	59	62
9	60	62
H= 6 K= 2		
0	94	87
1	11	16
2	176	181
3	35	31
4	38	31
5	161	160
6	41	42
7	55	56
8	9	8
9	8	6
H= 6 K= 3		
0	21	24
1	77	73
2	53	56
3	158	163
4	102	103
5	121	118
6	76	73
7	52	49
8	45	46
H= 6 K= 4		
0	118	121
1	118	119
2	130	132
3	125	124
4	79	80
5	35	29
6	28	27
7	45	44
8	48	48
H= 6 K= 5		
0	103	100
1	106	108
2	41	42
3	71	72
4	29	28
5	116	116
6	41	40
7	9	13
H= 6 K= 6		
0	222	223
1	75	76
2	152	149
3	57	60
4	45	44
5	33	29
6	114	115
7	25	23
H= 6 K= 7		
0	74	77
1	154	152
2	35	33
3	26	25
4	9	9
5	94	94
H= 6 K= 8		
0	114	115
1	78	78
2	52	53
3	38	37
4	68	68
H= 6 K= 9		
0	72	70
1	73	70
H= 7 K= 0		
1	162	171
2	50	49
3	10	10
4	26	28
5	52	55
6	9	7
H= 7 K= 1		
0	40	40
1	10	19
2	72	75
3	107	109
4	67	66
5	35	29
6	43	46
H= 7 K= 2		
0	10	11
1	72	77
2	98	102
3	49	50
4	48	48
5	31	31
6	68	69
H= 7 K= 3		
0	115	116
1	50	48
2	137	139
3	72	79
4	115	118
5	133	133
H= 7 K= 4		
0	48	51
1	82	88
2	9	10
3	45	42
4	120	119
5	56	51
H= 7 K= 5		
0	9	4
1	69	70
2	51	48
3	21	21
4	89	87
H= 7 K= 6		
0	9	3
1	100	101
2	51	52

---

* Note that the x,y,z directions defined by Berthou *et al.* correspond to our y,z,x. The atom nomenclature in this paper conforms to that of Craven *et al.* (1969) rather than Berthou *et al.* (1962, 1965).

Table 2. Atomic parameters with estimated standard deviations

Positional parameters are given as fractions of the lattice translations. Thermal parameters are given according to the expression:

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

The e.s.d.'s given in parentheses refer to the least significant figures in the parameter values.

	x	y	z	B or β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Na	0·07429 (10)	0·17176 (5)	0·49220 (4)	0·01317 (13)	0·00473 (4)	0·00361 (3)	0·00070 (6)	0·00176 (6)	0·00004 (3)
N(1)	0·4317 (2)	0·0617 (1)	0·2865 (1)	0·0075 (3)	0·0061 (1)	0·0045 (1)	0·0000 (1)	−0·0002 (1)	−0·0021 (1)
H(1)	0·294 (4)	−0·055 (2)	0·290 (2)	4·6 (6)					
C(2)	0·5174 (2)	0·1264 (1)	0·3697 (1)	0·0099 (3)	0·0037 (1)	0·0032 (1)	−0·0002 (2)	0·0001 (1)	−0·0008 (1)
O(2)	0·4034 (2)	0·1748 (1)	0·4341 (1)	0·0099 (2)	0·0052 (1)	0·0041 (1)	0·0003 (1)	0·0012 (1)	−0·0020 (1)
N(3)	0·7157 (2)	0·1359 (1)	0·3795 (1)	0·0094 (2)	0·0047 (1)	0·0034 (1)	−0·0008 (1)	−0·0002 (1)	−0·0009 (1)
C(4)	0·8331 (2)	0·0843 (1)	0·3062 (1)	0·0096 (3)	0·0041 (1)	0·0034 (1)	−0·0002 (2)	−0·0003 (1)	−0·0003 (1)
O(4)	1·0165 (2)	0·0869 (1)	0·3200 (1)	0·0056 (2)	0·0076 (1)	0·0054 (1)	−0·0007 (1)	−0·0004 (1)	−0·0014 (1)
C(5)	0·7561 (2)	0·0260 (1)	0·2026 (1)	0·0093 (3)	0·0052 (1)	0·0033 (1)	−0·0004 (2)	−0·0005 (1)	−0·0010 (1)
C(6)	0·5314 (2)	0·0115 (1)	0·2037 (1)	0·0093 (3)	0·0050 (1)	0·0040 (1)	0·0010 (2)	−0·0008 (2)	−0·0015 (1)
O(6)	0·4439 (2)	−0·0411 (1)	0·1328 (1)	0·0129 (3)	0·0085 (1)	0·0057 (1)	−0·0004 (2)	−0·0017 (1)	−0·0042 (1)
C(7)	0·8517 (3)	−0·0907 (2)	0·1936 (1)	0·0118 (4)	0·0065 (1)	0·0054 (1)	−0·0022 (2)	−0·0001 (2)	−0·0024 (1)
H(71)	0·807 (3)	−0·126 (2)	0·125 (2)	3·1 (4)					
H(72)	0·994 (3)	−0·083 (2)	0·180 (2)	3·4 (4)					
C(8)	0·8076 (4)	−0·1647 (2)	0·2908 (2)	0·0281 (6)	0·0055 (1)	0·0086 (2)	0·0020 (3)	0·0008 (3)	−0·0003 (1)
H(81)	0·867 (3)	−0·131 (2)	0·353 (2)	4·0 (5)					
H(82)	0·667 (5)	−0·173 (2)	0·305 (2)	7·3 (8)					
H(83)	0·852 (4)	−0·243 (2)	0·280 (2)	6·8 (8)					
C(9)	0·8117 (3)	0·0982 (2)	0·1011 (1)	0·0169 (4)	0·0077 (1)	0·0036 (1)	0·0002 (2)	0·0009 (2)	−0·0004 (1)
H(91)	0·777 (3)	0·054 (2)	0·039 (2)	3·6 (5)					
H(92)	0·954 (3)	0·104 (2)	0·101 (2)	3·5 (5)					
C(10)	0·7167 (4)	0·2129 (2)	0·0987 (2)	0·0290 (6)	0·0082 (2)	0·0059 (1)	0·0012 (3)	0·0003 (3)	0·0018 (1)
H(101)	0·563 (4)	0·209 (2)	0·089 (2)	5·5 (6)					
H(102)	0·748 (4)	0·260 (3)	0·031 (2)	6·5 (7)					
H(103)	0·750 (3)	0·257 (2)	0·165 (2)	4·1 (5)					

We have independently confirmed these results by solving the phase problem using direct methods. The origin and enantiomorph determining phases were assigned as follows:

No.*	h	k	l	$\|E\|$	α
2	0	9	5	2·75	$\pi/2$
3	1	0	13	2·72	$\pi/2$
7	5	0	6	2·51	0
12	0	4	3	2·30	0

In addition, five phases could be estimated by symbolic addition:

1	2	0	7	2·88	$-\pi/2$
13	1	9	7	2·27	$\simeq 0$
14	0	3	3	2·27	$\pi/2$
20	0	13	3	2·13	$-\pi/2$
37	0	2	2	1·97	π

After a tangent refinement, an E map based on 153 phased reflections with $|E| > 1·4$ showed all 14 heavy atoms. The R value at this stage was 0·185.

The refinement of the atomic parameters was done by the least-squares block-diagonal program for IBM 1130 computer (Shiono, 1968). The X-ray atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1962) for the heavy atoms, and from Stewart, Davidson & Simpson (1965) for the hydrogen atoms. The sodium ion was treated as an atom with $Z = 11$. The function minimized in the refinement was $\Sigma \omega \Delta F^2$, using the weighting scheme $\sigma^2(F) = 1·3 + 0·01 F^2$. All mentioned R values are defined as $R = \Sigma |\Delta F_{\text{meas}}| / \Sigma |F_{\text{meas}}|$. The refinement reduced R to

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* This number is from the listing of reflections in decreasing order of $|E|$.

0·106 and 0·065 using individual isotropic and anisotropic thermal parameters respectively. At this stage, the hydrogen atoms were located in a difference electron density map. Refining with anisotropic thermal parameters for the heavy atoms and isotropic ones for the hydrogen atoms gave convergence at $R = 0·030$ (0·032) for the observed (all) reflections. Comparison of observed and calculated structure amplitudes showed systematic differences which might be explained as extinction effects. After excluding all eight reflections with $|F_c| > 60$ and $\sin \theta \leq 0·3$, the final R value became 0·024 (0·025) and the R_w value 0·033 (0·037) with $[\Sigma(\Delta F_{\text{meas}}/\sigma_F)^2/(m-n)]^{1/2} = 0·81$. The observed and calculated structure factors are given in Table 1 and the final atomic positional and thermal parameters are shown in Table 2. In Fig. 1, the thermal parameters are represented as 50% probability ellipsoids.

The best least-squares fit of atomic anisotropic thermal parameters U_{ij} to a rigid-body motion (Schomaker & Trueblood, 1968) gave the parameters which are listed in Table 3. The rigid-body model is only partially satisfactory, since about one half of the calculated rigid body U_{ij} values differ from the corresponding input U_{ij} values by more than three times the estimated standard deviations in the input U_{ij}. The poorest least-squares fit is for the terminal methyl carbon atoms. The greatest difference in an individual parameter is for U_{33} of carbon C(10) (0·0092 Å^2 with σ of 0·0009 Å^2).

The bond length corrections assuming rigid body motion are about 0·005 Å in the pyrimidine ring and 0·007 Å in the ethyl groups (Table 4). The corrections for the ring bond lengths are in the expected range, but the corrected C(7)–C(8) and C(9)–C(10) bond lengths (1·511, 1·518 Å) are still somewhat short of the expected value (1·526 Å; Lide, 1962), but these bonds in-

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Table 3. *Rigid body vibrational tensors*

The tensors L for libration, T for translation, and S for screw motion, are referred to the right-handed orthogonal molecular axes in the direction of

(1) the bond C(5)–C(2)
(2) the normal to the pyrimidine ring of the side of atom C(9)
(3) the cross product of (1) and (2).

The origin, defined by symmetrizing S, has the coordinates 0·822 Å, −0·191 Å, 0·080 Å referred to the cetner of mass and in the L-system. Criteria for the rigid body fit:

$$[\Sigma\{U_{ij}(\text{meas}) - U_{ij}(\text{calc})\}^2/(n-s)]^{1/2} = 0·0029 \text{ Å}^2$$
$$\text{e.s.d. of } U_{ij} = 0·0034 \text{ Å}^2$$

		(1)	(2)	(3)
L and direction cosines	4·75°	−0·441	−0·498	0·747
	3·51	−0·896	−0·199	−0·397
	2·16	−0·049	−0·844	0·534
T and direction cosines	0·170 Å	−0·029	0·835	−0·550
	0·150	−0·506	0·462	0·728
	0·133	0·862	0·300	0·409
S and direction cosines	0·001	−0·001	−0·156	−0·988
	0·000	0·969	0·245	−0·040
	−0·001	0·248	−0·957	0·151

volve the atoms for which departures from rigid body mition are greatest.

Table 4. *Intra- and intermolecular distances and angles*

The bond lengths between heavy atoms within the barbital ion are listed as
(1) uncorrected distances
(2) distances with corrections based on the rigid body mode of molecular thermal motion.
Estimated standard deviations are as follows:

C–N, C–O, C–C bonds within the ring, and Na–O distances	0·002 Å
C–C bonds in the aliphatic chain	0·003–4 Å
N–H, C–H bonds	0·04 Å
C–N–O angles and angles between heavy atoms at the ring	0·3°
C–C–C angles in the chain	0·5°
C–N–H angles	2°
Other angles with H atoms	4°

Symmetry code

	x	y	z
a	$-1+x$	y	z
b	$1-x$	$\frac{1}{2}+y$	$\frac{1}{2}-z$
c	$\frac{3}{2}-x$	$-y$	$\frac{1}{2}+z$
d	$1+x$	y	z

Table 4 (*cont.*)

	x	y	z
e	$\frac{1}{2}-x$	$-y$	$-\frac{1}{2}+z$
f	$2-x$	$\frac{1}{2}+y$	$\frac{1}{2}-z$
g	$1-x$	$-\frac{1}{2}+y$	$\frac{1}{2}-z$
h	$\frac{3}{2}-x$	$-y$	$\frac{1}{2}+z$
i	$2-x$	$-\frac{1}{2}+y$	$\frac{1}{2}-z$
k	$\frac{3}{2}-x$	$-y$	$-\frac{1}{2}+z$
l	$\frac{1}{2}-x$	$-y$	$\frac{1}{2}+z$
m	$-\frac{1}{2}+x$	$\frac{1}{2}-y$	$1-z$

| (i) Bond lengths	(1)	(2)
N(1)–C(2)	1·396 Å	1·401 Å
C(2)–N(3)	1·343	1·349
N(3)–C(4)	1·339	1·343
C(4)–C(5)	1·527	1·533
C(5)–C(6)	1·520	1·527
C(6)–N(1)	1·348	1·351
C(5)–C(7)	1·538	1·545
C(5)–C(9)	1·549	1·557
C(7)–C(8)	1·504	1·511
C(9)–C(10)	1·512	1·518
C(2)–O(2)	1·238	1·241
C(4)–O(4)	1·245	1·250
C(6)–O(6)	1·216	1·221
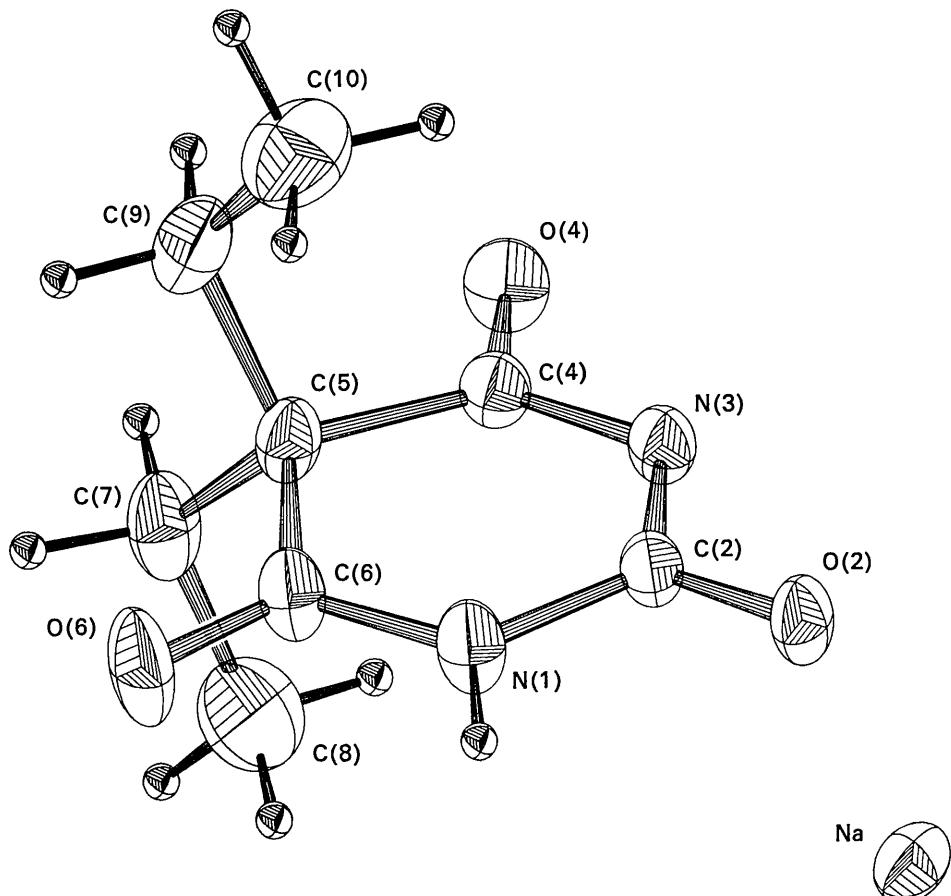
Fig. 1. The 50% probability ellipsoidal representation of atomic thermal parameters of sodium barbital (Johnson, 1965).

Table 4 (cont.)

(ii) Bond angles

C(7)—C(5)-C(4)	109·3°		H(82)—C(8)—H(83)	102°
C(9)—C(5)-C(5)	108·1		H(83)—C(8)—C(7)	113
			H(91)—C(9)—C(5)	105
H(1)—N(1)-C(2)	115		H(91)—C(9)—C(10)	113
H(1)—N(1)-C(6)	119		H(91)—C(9)—H(92)	107
H(71)-C(7)—C(5)	109		H(92)—C(9)—C(5)	106
H(71)-C(7)-C(8)	111		H(92)—C(9)—C(10)	111
H(71)-C(7)-H(72)	101		H(101)-C(10)—C(9)	113
H(72)-C(7)-C(5)	110		H(101)-C(10)-H(102)	98
H(72)-C(7)-C(8)	113		H(101)-C(10)-H(103)	110
H(81)-C(8)-C(7)	107		H(102)-C(10)-C(9)	115
H(81)-C(8)-H(82)	108		H(102)-C(10)-H(103)	108
H(81)-C(8)-H(83)	113		H(103)-C(10)-C(9)	112
H(82)-C(8)-C(7)	113			

(iii) Hydrogen bonding distances and angles

N(1)-O(4)d	2·837 Å		N(1)-H(1)-O(4)d	162°
H(1)-O(4)d	1·938		N(1)···O(4)d-C(4)d	160·5

(iv) Sodium coordination tetrahedra

Na-O(2)	2·322 Å		O(2)——Na-O(2')m	124·8°
Na-O(6)l	2·315		O(2)——Na-O(4)a	84·0
Na-O(2')m	2·341		O(2)——Na-O(6)l	106·5
Na-O(4)a	2·354		O(2')m-Na-O(4)a	126·5
			O(2')m-Na-O(6)l	102·8
			O(4)a——Na-O(6)l	110·8

(v) Close intermolecular approaches

Na—N(3)a	2·80 Å		H(71)—O(2)g	2·87 Å
O(2)-O(4)a	3·13		H(72)—H(1)d	2·93
O(4)-H(81)f	2·52		H(81)—H(91)h	2·61
O(6)-H(72)a	3·13		H(82)—H(101)g	2·45
N(1)-H(83)b	3·12		H(83)—O(4)i	2·52
C(2)-H(91)c	3·28		H(91)—H(81)k	2·61
N(3)-H(71)c	2·98		H(92)—H(83)f	2·66
C(4)-Nad	2·97		H(101)-H(82)b	2·45
C(5)-H(1)d	3·78		H(102)-H(81)k	2·76
C(6)-Nae	3·45		H(103)-H(83)f	2·76
H(1)-H(83)b	2·73			

Discussion

(i) The barbital ion

The conformation of the barbital ion (Fig. 1) is similar to that of barbital itself, *i.e.* the ring is nearly planar and the ethyl groups together with C(5) form a hydrocarbon chain which is nearly in the all *trans* configuration, with the chain axis perpendicular (90·2°) to the ring plane. Deviations from the idealized geometry are given in Table 5 as atomic displacements from best least-squares planes and torsion angles about covalent bonds.

Table 5. *Best least-squares planes and torsion angles of pyrimidine ring*

Plane 1: Plane through the six pyrimidine ring atoms.
Plane 2: See plane 1 and the three adjacent O atoms.
Plane 3: Plane through the atoms of the chain C(5), C(7), C(8), C(9), C(10).

(i) Equations of the planes:
Plane 1: $-0.047X$ $+0.838Y$ $-0.544Z = -1.375$
Plane 2: $-0.007X$ $+0.826Y$ $-0.564Z = -1.301$
Plane 3: $0.799X$ $+0.354Y$ $+0.486Z = 5.352$

Table 5 (cont.)

(ii) Distances (Å) of atoms from the planes. The underlined values belong to atoms *not* forming the planes.

	Plane 1	Plane 2	Plane 3
N(1)	-0·032	-0·069	
C(2)	0·041	-0·003	
N(3)	0·009	0·014	
C(4)	-0·061	-0·000	1·285
C(5)	0·062	0·135	0·014
C(6)	-0·020	-0·004	-1·249
C(7)			-0·019
C(8)			0·002
C(9)			0·021
C(10)			-0·018
O(2)	0·136	0·040	
O(4)	-0·183	-0·078	
O(6)	-0·053	-0·034	
H(1)	-0·075	-0·149	

(iii) Torsion angles within the pyrimidine ring

Bond vector	Torsion angle
N(1)-C(2)	6·17°
C(2)-N(3)	-1·64
N(3)-C(4)	-7·70
C(4)-C(5)	11·98
C(5)-C(6)	-7·24
C(6)-N(1)	-0·85

Table 5 (cont.)

(iv) Torsion angles including atoms of the hydrocarbon chain

C(9)–C(5)–C(7)–C(8)	182·2°
C(7)–C(5)–C(9)–C(10)	183·0
N(3)–C(4)–C(5)–C(7)	132·4
N(3)–C(4)–C(5)–C(9)	252·5
N(1)–C(6)–C(5)–C(7)	231·9
N(1)–C(6)–C(5)–C(9)	112·5

In Fig. 2, bond lengths and angles for the barbital ion are compared with those of barbital. As expected, these are very similar for the C–C bonds at C(5) and in the ethyl groups, and are most significantly different in the region near atom N(3) which is the deprotonation site. As a result of deprotonation, the internal ring
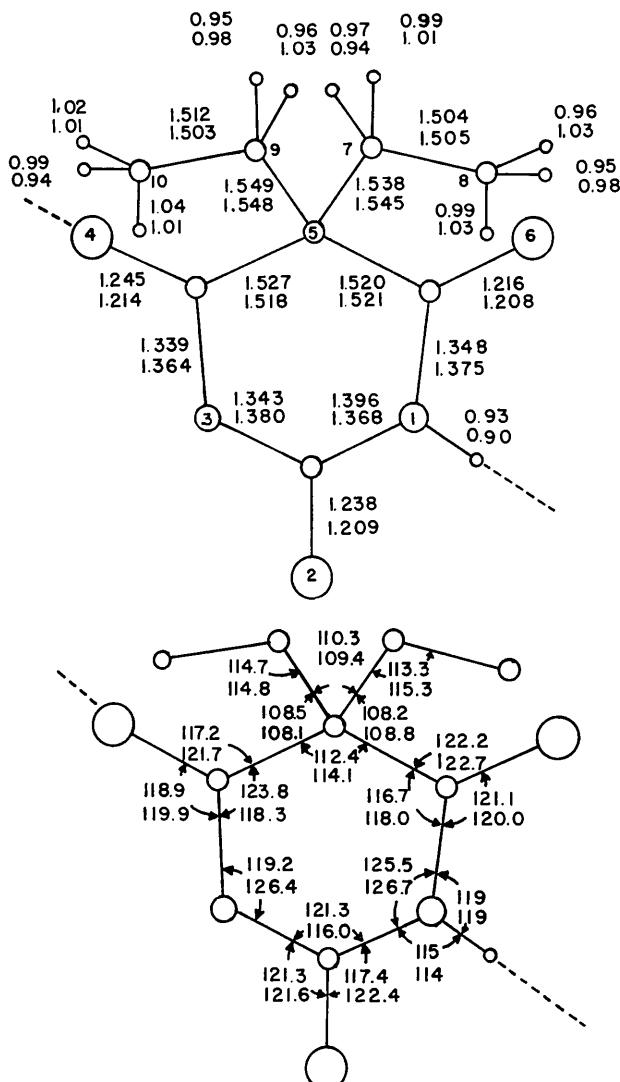
Fig. 2. Bond lengths (Å) and bond angles (°) for the barbital ion (upper number) and the barbital molecule (lower number). The latter are average values of three molecules: Barbital I (Craven et al., 1969) and the 2:1 complex of barbital and caffeine (Craven & Gartland, 1970). The e.s.d.'s are between 0·002 and 0·004 Å and 0·3 and 0·6°.

angle at N(3) closes from 126·4° in barbital to 119·2° in its ion. A similar effect has been noted by Singh (1965) in a variety of pyrimidine crystal structures. The opening of each of the internal ring angles at the adjacent carbon atoms C(2) and C(4) by 5° over-compensates for the closing of the angle at N(3) by 7°. This suggests that all three angular changes are a consequence of the deprotonation.

In the barbital ion, the two C–N bonds at the deprotonated nitrogen atom are almost equal and significantly shorter (1·34 Å) than the corresponding bonds in barbital (1·36 and 1·38 Å). Conversely, the flanking carbonyl bonds C(4)–O(4) and C(2)–O(2) are significantly longer (1·24 vs. 1·21 Å). These results and the approximate symmetry about N(3) in the O(4)–C(4)–N(3)–C(2)–O(2) grouping indicate that the greatest part of the formal negative charge on the barbital ion is distributed almost equally between the O(2) and O(4) oxygen atoms. The two C–N(1) bond lengths from the non-deprotonated nitrogen atom N(1) differ significantly (1·40 vs. 1·35 Å).

(ii) Ionic interactions and hydrogen bonding

The sodium ions are tetrahedrally coordinated by four oxygen atoms from four different barbital ions (Fig. 3). The geometry of this tetrahedron is nearly regular, with Na···O distances ranging between 2·32 and 2·35 Å and the O···Na···O angles ranging between 84 and 127° (Table 4). The Na···O distances are close to the sum of the ionic radii (2·4 Å; Pauling, 1960). The tetrahedra share corners at O(2) and form infinite chains in the a direction.

There is only one crystallographically distinct hydrogen bond, N(1)–H···O(4), in the sodium barbital crystal structure and this links barbital ions in continuous ribbons parallel to a. The atoms N(1)–H(1)···O(4)–C(4) in the hydrogen bond are almost collinear, as shown by the angles in Table 4 (iii). This geometry seems to be typical of barbiturate crystal structures in which two molecules are linked by only one hydrogen bond, e.g. γ-methylamobarbital (Gartland & Craven, 1971) and the 2:1 complex of barbital with caffeine (Craven & Gartland, 1970).

The intermolecular interactions involving each barbital oxygen atom are as follows: oxygen O(2) is coordinated to two different sodium ions, oxygen O(4) is coordinated to one sodium ion and is acceptor for a hydrogen bond, and oxygen O(6) is coordinated to one sodium ion. These interactions are qualitatively stronger for O(2) and O(4) than for O(6). They appear to be compatible with the conclusion based on intramolecular bond lengths and angles that the greater part of the formal negative charge on the barbital ion is at O(2) and O(4).

(iii) Comparison of the crystal structures of barbital I and sodium barbital

The similarity between the broad features of these two crystal structures is best seen by comparing the

views down the ribbons of molecules (ions) which are linked by N(1)–H···O(4) hydrogen bonds (Fig. 4, and Craven *et al.*, 1969, Fig. 5). The lattice translations along the ribbon directions are nearly the same (6·72 *vs* 6·83 Å) as are the N(1)···O(4) hydrogen bond distances (2·84 *vs* 2·87 Å). In barbital I these ribbons
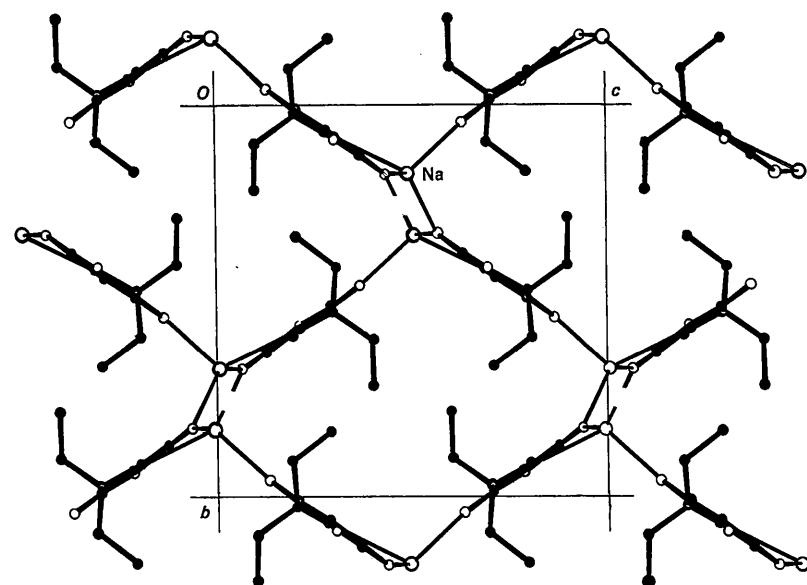
Fig. 3. The crystal structure of sodium barbital as a projection down the *a* axis. The coordination bonding between the barbital ions and the sodium ion.
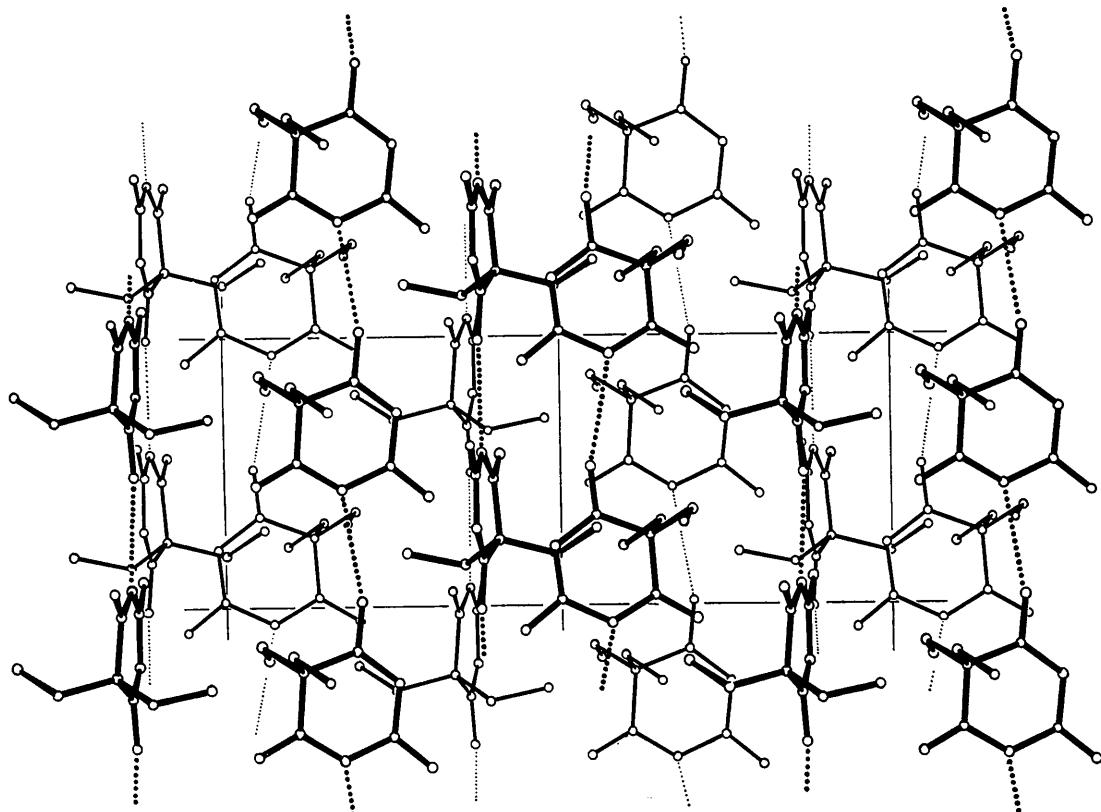
Fig. 4. The crystal structure of sodium barbital as a projection along [011]. The hydrogen bonding system.

are further cross-linked by pairs of hydrogen bonds N(3)–H···O(2) to form doubly stranded ribbons. In sodium barbital, the second hydrogen atom is not available for hydrogen bonding, but a similar cross-linking is effected by ionic interactions involving sodium ions. It should be noted however that N(3) is not in the immediate coordination shell about the sodium ion. The closest Na···N(3) distance is 2·80 Å.

The assembly of hydrogen bonded ribbons in barbital I leads to a close association among the ethyl groups which project into 'hydrophobic channels' surrounding the threefold screw axes and threefold inversion axes. Similar channels are found in sodium barbital running parallel to a (Fig. 3). There are four H···H distances within 0·2 Å of the sum of the van der Waals radii (2·4 Å, Pauling, 1960) as shown in Table 4(v).

(iv) *Comparison between the crystal structures of sodium and potassium barbital*

The replacement of sodium by potassium gives non-uniform increases in the cell translations ($\Delta a = 0·11$, $\Delta b = 0·40$ and $\Delta c = 0·84$ Å) which seem to arise from the increase in alkali ionic radii and a slight reorientation of the barbital ion. The average increase in observed metal–oxygen distances is 0·33 Å, which is close to the expected difference in ionic radii (0·37 Å; Pauling, 1960). The NH···O–C hydrogen bond is stretched by 0·14 Å (2·98 vs 2·84 Å) in the potassium salt. Both the hydrogen bonded ribbons and columns of metal–oxygen tetrahedra are parallel to a. The resistance of the hydrogen bonds to further stretch is probably the reason for the smallest lattice expansion being in the a direction. The relative expansion of metal–oxygen tetrahedra and hydrogen bonding along a is associated with a twisting of the barbital ion. The angle between a and the molecular axis N(1) → C(4) decreases from 7·6° in the sodium salt to 3·7° in the potassium salt. There is a smaller decrease in the dihedral angle between best least-squares planes through the barbital rings in adjacent hydrogen bonded ribbons (66·1° vs 65·5°). The expansion of b and c lattice translations is attributed to the expansion of metal oxygen tetrahedra and adjustment to accommodate the ethyl groups. The tilting of the barbital ion brings the plane of the alkyl group carbon atoms more nearly parallel to

(100) in such a way that lattice expansion would be greater along b than c, as is in fact observed.

A comparison of the molecular geometry of the barbital ion in the sodium and potassium salts shows no significant differences in terms of the respective average standard deviations in atomic positions (0·002 and 0·05 Å).

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