for it to be possible for the transition to a polymer to occur spontaneously within the solid. Thus, it seems more likely that the polymerization is a surface phenomenon, involving free radicals, and that it slowly affects the entire crystal.

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A Barbiturate Without Hydrogen Bonding: The Crystal Structure of Sodium 1-Methyl-5,5-diethylbarbiturate (Sodium Metharbital)

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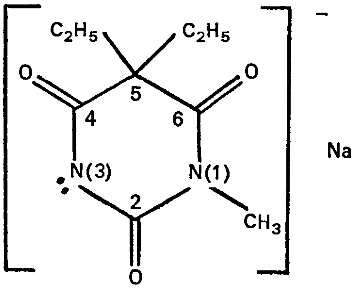
The crystal structure of sodium 1-methyl-5,5-diethylbarbiturate $Na.C_9N_2O_3H_{13}$ (also called sodium metharbital or sodium gemonil) has been determined from X-ray data measured on an automatic diffractometer. The crystal data are: space group $Pna2_1$, $a=12{\cdot}670$ (3), $b=10{\cdot}796$ (2), $c=7{\cdot}802$ (2) Å, $Z=4$, $D_m=1{\cdot}369$ g.cm^{-3}. The final R is 0·023. The conformation of the metharbital ion is similar to the conformations of the barbital ion and the barbital molecule. Methylation of the pyrimidine ring at N(1) and deprotonation at N(3) decrease the internal bond angles at N(1) and N(3) by approximately 4–5° each. In the absence of hydrogen bonding, the dominant role in crystal packing is played by ionic coordination interactions. The sodium ion is fivefold coordinated by four oxygen atoms and the deprotonated nitrogen atom. The extremely short Na–N distance of 2·42 Å suggests that this nitrogen atom carries a great part of the formal negative charge of the metharbital anion.

Introduction

In the crystal structures of barbiturates determined so far, hydrogen bonding seems to play the dominant role in packing the barbiturate molecules or ions. Depending on the type of compound (free barbituric acid, salt, or complex), other intermolecular interactions may also be important: the requirements of effective packing of the alkyl groups (Gartland & Craven, 1971), $C{=}O\cdots C{=}O$ dipole-dipole interactions (Prout & Wallwork, 1966), and coordination of cations (Berking & Craven, 1971; Berking, 1971*a*,*b*).

In those barbiturates in which the hydrogen atoms at C(5) are substituted, the imino nitrogen atoms N(1) and N(3) in the pyrimidine ring serve as donors (or if deprotonated, as acceptors), and the exocyclic oxygen atoms serve as acceptors for hydrogen-bonding in a variety of ways.

The crystal structure of sodium 1-methyl-5,5-diethylbarbiturate (also called sodium metharbital or sodium gemonil) was determined because here, N(1) being methylated and N(3) being deprotonated, hydrogen-bonding is *a priori* impossible. Therefore the other binding types mentioned above are dominant. The results have already been reported briefly (Berking, 1971*c*).



Experimental

Sodium metharbital was prepared by adding sodium hydroxide and metharbital in ethanol solution. Crystals were transparent and prismatic, the longest dimension being along the *c* axis. X-ray reflections were absent for $0kl$ $(k+l=2n+1)$ and $h0l$ $(h=2n+1)$. The density was measured by flotation in a mixture of chloroform and *n*-hexane. The crystal data are:

Space group: $Pna2_1$ (from systematic absences)
M.W. 220·20
$a=12{\cdot}670(3)$, $b=10{\cdot}796(2)$, $c=7{\cdot}802(2)$ Å
$V=1067{\cdot}97$ Å^3, $Z=4$
$D_m=1{\cdot}369$, $D_x=1{\cdot}370$ g.cm^{-3}.

The lattice parameters and X-ray intensities were measured on a Picker FACS I automatic diffractometer, using Cu $K\alpha$ radiation and a graphite monochromator. The crystal, with dimensions $0{\cdot}2\times0{\cdot}1\times0{\cdot}1$ mm, was mounted with *c* along the diffractometer φ axis. Intensities for 962 independent reflections (each intensity being measured at least twice) were measured in the θ–2θ scanning mode up to $2\theta=130°$. Of these, 73 reflections were considered to be 'unobserved', because their net intensities did not exceed three times the standard deviation estimated from counting statistics. Absorption corrections were not applied.

Table 1. $|F_o|$ *and* $|F_c|$ *multiplied by* 10

Unobserved reflections are indicated by *; reflections affected by extinction and not included in the final refinement are indicated by +.

L= 0 K= 0		
2	888+	1038
4	867+	900
6	189	200
8	52	50
10	95	94
12	157	156
14	76	77
L= 0 K= 1		
1	548+	571
2	13	16
3	33	33
4	6*	12
5	131	124
6	44	42
7	48	48
8	86	84
9	205	198
10	30	34
11	63	60
12	31	29
13	62	61
14	10*	3
L= 0 K= 2		
0	113	108
1	897+	984
2	731+	767
3	329	340
4	306	296
5	214	221
6	21	25
7	215	217
8	113	113
9	78	77
10	204	197
11	101	103
12	38	38
13	117	114
14	55	53
L= 0 K= 3		
1	418	425
2	1072+	1154
3	86	83
4	284	285
5	106	107
6	388	394
7	270	270
8	57	56
9	82	79
10	12*	38
11	145	141
12	39	38
13	30	29
14	9*	14
L= 0 K= 4		
0	229	237
1	281	280
2	417	432
3	455	438
4	59	55
5	422	419
6	271	270
7	57	58
8	72	74
9	11*	29
10	11*	12
11	63	63
12	171	164
13	41	40
14	9*	12
L= 0 K= 5		
1	61	55
2	106	99
3	556	563
4	31	32
5	321	322
6	106	107
7	43	46
8	151	152
9	72	69
10	99	99
11	64	59
12	10*	10
13	80	78
L= 0 K= 6		
0	61	63
1	23	20
2	255	254
3	25	19
4	305	310
5	9*	17
6	351	344
7	106	103
8	78	78
9	11*	14
10	118	112
11	11*	11
12	131	132
L= 0 K= 7		
1	18	10
2	83	78
3	140	140
4	168	171
5	346	345
6	195	190
7	254	250
8	41	43
9	191	183
10	11*	16
11	10*	7
12	61	60
L= 0 K= 8		
0	10*	14
1	176	175
2	154	158
3	67	67
4	35	38
5	220	223
6	82	85
7	266	261
8	155	158
9	43	42
10	69	68
11	83	84
L= 0 K= 9		
1	67	67
2	66	67
3	106	107
4	60	62
5	12*	30
6	70	69
7	50	49
8	97	98
9	83	83
10	70	72
L= 0 K= 10		
0	204	199
1	148	147
2	10*	13
3	30	31
4	26	20
5	52	51
6	82	84
7	60	66
8	102	102
L= 0 K= 11		
1	92	93
2	45	44
3	50	48
4	84	88
5	56	59
6	26	26
7	39	43
L= 0 K= 12		
0	43	40
1	26	31
2	21	12
3	98	96
4	61	59
L= 1 K= 0		
2	299	296
4	293	292
6	440	448
8	220	215
10	143	147
12	113	111
14	135	130
L= 1 K= 1		
0	785+	834
1	220	225
2	213	231
3	345	357
4	173	167
5	363	369
6	230	232
7	333	333
8	149	147
9	10*	9
10	65	66
11	53	58
12	78	77
13	101	100
14	55	57
L= 1 K= 2		
1	283	282
2	443	466
3	391	399
4	630	652
5	317	316
6	311	315
7	165	160
8	236	243
9	140	134
10	74	75
11	81	84
12	133	135
13	71	69
14	51	48
L= 1 K= 3		
0	107	107
1	551	568
2	173	182
3	346	338
4	224	234
5	550	543
6	68	66
7	306	304
8	98	104
9	71	71
10	154	151
11	148	150
12	91	91
13	91	89
14	70	70
L= 1 K= 4		
1	182	185
2	520	524
3	248	249
4	319	308
5	295	289
6	241	247
7	42	41
8	81	77
9	76	75
10	122	119
11	65	67
12	56	56
13	10*	14
L= 1 K= 5		
0	122	125
1	45	44
2	144	138
3	452	452
4	137	141
5	90	94
6	38	36
7	63	58
8	160	164
9	142	139
10	168	170
11	11*	10
12	11*	23
13	88	85
L= 1 K= 6		
1	351	360
2	261	262
3	265	263
4	193	198
5	257	264
6	103	105
7	126	124
8	125	122
9	53	56
10	89	89
11	91	90
12	117	112
L= 1 K= 7		
0	177	176
1	147	142
2	9*	5
3	119	116
4	63	62
5	93	95
6	89	90
7	190	187
8	11*	4
9	64	66
10	48	48
11	43	44
12	70	69
L= 1 K= 8		
1	78	75
2	113	113
3	129	130
4	157	153
5	115	118
6	89	88
7	127	124
8	128	130
9	83	80
10	10*	7
11	74	71
L= 1 K= 9		
0	70	72
1	174	174
2	80	78
3	143	143
4	86	85
5	99	99
6	75	77
7	12*	29
8	105	105
9	97	97
10	48	44
L= 1 K= 10		
1	43	43
2	164	161
3	73	71
4	80	77
5	104	103
6	52	52
7	117	117
8	10*	13
L= 1 K= 11		
0	96	93
1	66	66
2	62	60
3	42	42
4	11*	24
5	83	83
6	9*	11
7	102	99
L= 1 K= 12		
1	44	42
2	42	41
3	27	25
4	62	62
L= 2 K= 0		
0	816+	835
2	624+	652
4	498	509
6	115	117
8	174	174
10	240	236
12	216	214
14	75	76
L= 2 K= 1		
1	447	456
2	329	326
3	57	60
4	121	115
5	165	155
6	106	100
7	106	108
8	168	168
9	183	176
10	11*	26
11	270	266
12	137	133
13	84	88
14	92	94
L= 2 K= 2		
0	181	187
1	285	279
2	123	127
3	100	92
4	365	374
5	34	32
6	8*	9
7	82	84
8	139	138
9	97	101
10	308	306
11	183	181
12	119	117
13	156	154
14	96	95
L= 2 K= 3		
1	109	112
2	425	427
3	279	271
4	304	285
5	217	214
6	96	99
7	102	101
8	128	124
9	285	281
10	89	91
11	108	107
12	33	38
13	63	58
L= 2 K= 4		
0	437	429
1	95	92
2	151	154
3	104	103
4	95	92
5	97	97
6	75	78
7	218	218
8	223	215
9	236	233
10	134	139
11	12*	28
12	78	79
13	71	70
L= 2 K= 5		
1	303	305
2	119	109
3	99	93
4	151	148
5	9*	13
6	127	128
7	186	186
8	181	178
9	174	179
10	65	66
11	148	146
12	79	83
13	78	75
L= 2 K= 6		
0	204	209
1	59	53
2	159	154
3	298	299
4	68	69
5	59	59
6	138	134
7	181	182
8	262	258
9	100	104
10	85	85
11	10*	13
12	42	40
L= 2 K= 7		
1	115	112
2	132	130
3	241	235
4	153	153
5	11*	24
6	125	126
7	113	108
8	147	150
9	123	122
10	60	62
11	10*	15
L= 2 K= 8		
0	99	96
1	69	68
2	136	130
3	48	46
4	151	156
5	216	212
6	119	115
7	99	99
8	127	123
9	52	53
10	40	39
L= 2 K= 9		
1	153	151
2	129	124
3	80	78
4	102	104
5	96	95
6	135	132
7	77	78
8	11*	23
9	9*	21
L= 2 K= 10		
0	129	131
1	32	40
2	117	114
3	142	141
4	75	74
5	11*	2
6	100	99
7	30	31
8	9*	13
L= 2 K= 11		
1	95	92
2	131	130
3	103	102
4	10*	22
5	61	64
6	40	39
L= 2 K= 12		
0	57	53
1	91	90
2	77	79
3	38	41
L= 3 K= 0		
2	596	598
4	384	370
6	253	247
8	194	189
10	168	167
12	65	68
L= 3 K= 1		
0	219	216
1	270	268
2	124	118
3	306	304
4	366	346
5	418	404
6	226	221
7	109	110
8	81	80
9	34	38
10	66	69
11	55	59
12	34	37
13	66	63
L= 3 K= 2		
1	124	118
2	179	178
3	202	191
4	368	361
5	200	189
6	417	419
7	70	69
8	69	72
9	75	75
10	31	25
11	106	109
12	81	82
13	10*	20
L= 3 K= 3		
0	337	343
1	114	109
2	103	95
3	544	534
4	331	328
5	38	41
6	9*	24
7	210	209
8	91	88
9	59	56
10	111	110
11	12*	31
12	11*	11
13	59	57
L= 3 K= 4		
1	185	175
2	320	305
3	89	93
4	238	244
5	204	200
6	192	183
7	65	65
8	105	104
9	253	250
10	64	64
11	39	47
12	10*	25
13	54	51
L= 3 K= 5		
0	462	456
1	323	322
2	200	196
3	201	203
4	51	50
5	161	156
6	67	69
7	64	72
8	11*	22
9	145	132
10	63	64
11	11*	15
12	61	62
L= 3 K= 6		
1	88	94
2	81	81
3	117	123
4	208	202
5	76	78
6	71	69
7	105	107
8	142	140
9	39	38
10	78	76
11	38	38
12	38	39
L= 3 K= 7		
0	145	143
1	111	112
2	159	155
3	120	119
4	100	95
5	102	96
6	40	43
7	207	205
8	11*	14
9	11*	17
10	31	30
11	53	46
L= 3 K= 8		
1	80	78
2	118	115
3	93	92
4	33	45
5	138	138
6	183	179
7	57	58
8	40	40
9	83	81
10	38	35
L= 3 K= 9		
0	9*	5
1	122	121
2	33	37
3	147	140
4	102	103
5	77	73
6	47	45
7	42	42
8	50	49
9	9*	15
L= 3 K= 10		
1	11*	10
2	79	81
3	133	131
4	65	62
5	86	85
6	62	59
7	37	38
L= 3 K= 11		
0	106	103
1	100	99
2	10*	24
3	56	57
4	58	58
5	37	38
L= 4 K= 0		
0	432	424
2	362	344
4	320	313
6	93	96
8	277	274
10	166	171
12	126	122
L= 4 K= 1		
1	291	286
2	341	336
3	269	271
4	79	84
5	187	180
6	173	174
7	165	165
8	179	175
9	43	49
10	128	122
11	141	140
12	48	49
13	87	87
L= 4 K= 2		
0	338	331
1	208	194
2	258	265
3	145	142
4	236	230
5	39	40
6	192	192
7	120	124
8	103	98
9	102	103
10	181	176
11	57	54
12	99	98
13	47	44
L= 4 K= 3		
1	305	304
2	249	254
3	85	82
4	202	197
5	144	142
6	183	177
7	85	84
8	144	140
9	161	158
10	34	43
11	46	42
12	87	83
L= 4 K= 4		
0	505	495
1	171	159
2	39	41
3	89	93
4	29	31
5	55	58
6	53	52
7	171	174
8	124	126
9	53	55
10	85	81
11	85	85
12	60	59
L= 4 K= 5		
1	321	319
2	107	103
3	88	91
4	87	86
5	152	147
6	80	85
7	161	159
8	92	90
9	106	107
10	34	36
11	87	82
L= 4 K= 6		
0	9*	17
1	161	163
2	219	215
3	131	127
4	54	59
5	151	146
6	58	60
7	67	65
8	78	72
9	11*	18
10	125	118
11	55	54
L= 4 K= 7		
1	177	172
2	175	168
3	116	117
4	152	150
5	145	145
6	11*	9
7	39	44
8	59	58
9	146	141
10	62	60
L= 4 K= 8		
0	106	104
1	42	43
2	27	22
3	89	92
4	144	140
5	123	119
6	45	44
7	82	81
8	76	72
9	46	43
L= 4 K= 9		
1	76	76
2	36	41
3	190	181
4	89	88
5	98	97
6	84	82
7	30	25
8	31	33
L= 4 K= 10		
0	132	126
1	61	62
2	65	66
3	53	53
4	59	59
5	45	44
6	9*	18
L= 4 K= 11		
1	30	32
2	54	57
3	54	50
L= 5 K= 0		
2	144	135
4	83	87
6	185	185
8	121	118
10	93	94
12	73	74
L= 5 K= 1		
0	278	266
1	103	100
2	137	135
3	168	163
4	44	43
5	49	45
6	105	108
7	236	238
8	114	115
9	192	191
10	163	165
11	91	89
12	54	58
L= 5 K= 2		
1	48	55
2	153	156
3	39	35
4	142	138
5	72	70
6	65	61
7	120	115
8	242	240
9	49	47
10	43	43
11	75	74
12	148	144
L= 5 K= 3		
0	10*	2
1	58	53
2	56	53
3	59	61
4	59	59
5	270	266
6	144	143
7	224	227
8	117	111
9	32	38
10	41	35
11	36	40
L= 5 K= 4		
1	66	67
2	127	131
3	58	60
4	71	69
5	167	167
6	219	215
7	211	210
8	11*	13
9	11*	26
10	67	66
11	70	73
L= 5 K= 5		
0	104	100
1	162	158
2	112	116
3	144	140
4	34	27
5	211	199
6	123	125
7	53	48
8	55	61
9	11*	21
10	65	66
L= 5 K= 6		
1	135	138
2	34	26
3	108	110
4	157	150
5	200	202
6	139	138
7	42	47
8	69	71
9	38	36
10	9*	10
L= 5 K= 7		
0	139	139
1	30	26
2	65	62
3	90	92
4	75	74
5	175	175
6	45	43
7	84	82
8	47	51
9	57	60
L= 5 K= 8		
1	59	56
2	90	94
3	11*	14
4	153	150
5	33	36
6	82	77
7	10*	23
8	9*	6
L= 5 K= 9		
0	130	127
1	11*	29
2	56	53
3	138	130
4	43	45
5	53	54
6	35	35
L= 5 K= 10		
1	86	86
2	104	105
3	59	62
L= 6 K= 0		
0	391	396
2	100	99
4	165	154
6	114	113
8	116	115
10	89	90
L= 6 K= 1		
1	112	113
2	200	206
3	123	119
4	137	139
5	162	155
6	62	66
7	127	128
8	86	88
9	183	178
10	66	71
11	65	69
L= 6 K= 2		
0	137	144
1	151	144
2	195	197
3	209	209
4	124	119
5	160	159
6	105	107
7	57	59
8	95	91
9	81	87
10	89	88
L= 6 K= 3		
1	114	108
2	135	135
3	122	121
4	216	209
5	63	65
6	111	109
7	99	103
8	73	77
9	76	74
10	63	61
L= 6 K= 4		
0	204	200
1	218	217
2	173	168
3	112	116
4	107	106
5	69	72
6	59	60
7	114	115
8	70	64
9	40	35
10	69	64
L= 6 K= 5		
1	100	99
2	118	117
3	197	190
4	50	54
5	127	131
6	41	37
7	30	34
8	56	52
9	46	43
L= 6 K= 6		
0	274	266
1	119	124
2	51	59
3	115	114
4	43	45
5	11*	21
6	85	83
7	47	48
8	40	43
L= 6 K= 7		
1	85	81
2	101	103
3	49	51
4	33	37
5	10*	23
6	64	65
7	68	67
L= 6 K= 8		
0	132	127
1	53	56
2	84	84
3	75	71
4	79	81
5	32	33
L= 6 K= 9		
1	92	90
2	79	84
3	10*	17
L= 7 K= 0		
2	408	407
4	88	94
6	71	70
8	61	59
L= 7 K= 1		
0	162	163
1	168	164
2	147	146
3	200	193
4	86	85
5	145	147
6	107	105
7	89	82
8	90	90
9	9*	13
L= 7 K= 2		
1	118	118
2	107	106
3	195	198
4	160	158
5	64	64
6	59	58
7	45	49
8	43	50
9	45	45
L= 7 K= 3		
0	312	311
1	154	148
2	114	116
3	94	98
4	146	143
5	160	152
6	95	96
7	10*	21
8	30	23
L= 7 K= 4		
1	80	78
2	68	65
3	91	89
4	145	138
5	106	104
6	48	48
7	68	74
8	66	65
L= 7 K= 5		
0	93	95
1	166	164
2	35	34
3	110	106
4	48	46
5	136	125
6	82	79
7	103	102
L= 7 K= 6		
1	78	76
2	78	80
3	121	119
4	113	109
5	10*	10
6	101	98
L= 7 K= 7		
0	94	95
1	56	58
2	72	72
3	57	57
4	81	81
L= 8 K= 0		
0	90	85
2	96	99
4	104	103
6	27	25
L= 8 K= 1		
1	77	78
2	53	53
3	110	113
4	82	79
5	71	68
6	72	70
L= 8 K= 2		
0	80	83
1	11*	19
2	101	97
3	66	67
4	11*	27
5	29	26
6	68	70
L= 8 K= 3		
1	102	105
2	101	99
3	58	55
4	38	40
5	68	73
6	23	15
L= 8 K= 4		
0	133	130
1	42	43
2	26	21
3	41	38
4	45	43
5	28	29
L= 8 K= 5		
1	86	86
2	51	50
3	34	36
L= 8 K= 6		
0	46	46
L= 9 K= 0		
2	74	77
L= 9 K= 1		
0	106	102
1	28	27

Structure determination and refinement

The phase problem was easily solved using direct methods. The assignment of origin- and enantiomorph-determining phases in space group $Pna2_1$ (type $1P220$ in the notation of Hauptman & Karle, 1955) is similar to that in space group $P2_1$ (type $1P202$). A tangent refinement with the starting phases:

No.	h	k	l	$\lvert E\rvert$	α
1	2	3	0	2·90	π
2	5	7	0	2·56	π
13	5	3	1	2·10	0
15	10	1	5	2·03	$0{\cdot}6\pi$

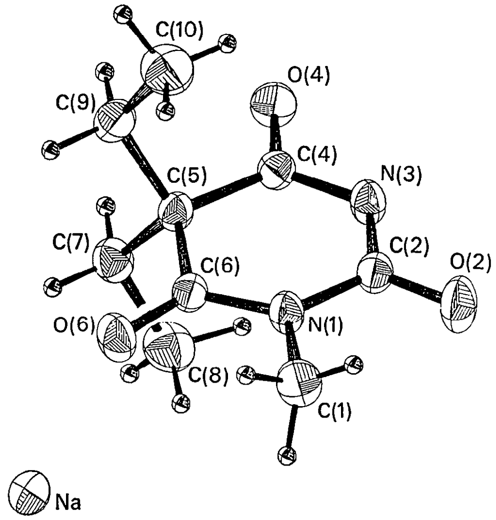


Fig. 1. The structure of sodium metharbital in the 50% probability ellipsoidal representation of the atomic thermal parameters (Johnson, 1965).

converged with $R_E=\sum||E_o|-|E_c||/\sum|E_o|=0{\cdot}20$ and yielded the phases for 146 reflections with $|E|>1{\cdot}36$. An E map, based on these phases, showed all 15 non-hydrogen atoms.

The atomic parameters were refined by full-matrix least-squares program *ORFLS* in the IBM 7090 version of Shiono (1966). 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 $Z=11$. Anomalous dispersion was applied for the sodium ($\Delta f'=0{\cdot}1$, $\Delta f''=0{\cdot}2$) and for the oxygen atoms ($\Delta f'=0{\cdot}0$; $\Delta f''=0{\cdot}1$). The function minimized was $\sum w\Delta^2$, using the empirical weighting scheme, $1/w=\sigma^2(F)=1{\cdot}25-0{\cdot}075F+0{\cdot}0015F^2$. The refinement reduced $R=\sum|\Delta F_{\text{meas}}|/\sum|F_{\text{meas}}|$) to 0·076 and 0·050, using individual isotropic and anisotropic thermal parameters respectively. At this stage, the hydrogen atoms were located from a difference electron density map.

Refinement with anisotropic thermal parameters for the heavy atoms and isotropic ones for the hydrogen atoms, and removing nine reflections which appeared to be affected by extinction, reduced the R value to 0·023 (0·027) for the observed (all) reflections, and R_w to 0·030 (0·030) with $[\sum w(\Delta F)^2/(m\text{-}n)]^{1/2}=1{\cdot}28$. The observed and calculated structure amplitudes are given in Table 1. The final atomic positional and thermal parameters are given in Table 2. The thermal parameters (Fig. 1) are represented as 50% probability ellipsoids (*ORTEP*, Johnson, 1965). The best least-squares fit of anisotropic thermal parameters to a rigid-body motion (Schomaker & Trueblood, 1968) was calculated and found to be satisfactory when the atoms of the two ethyl groups are omitted. Bond length corrections, assuming rigid-body motion, are about 0·005 Å (Table 3).

Table 2. *Atomic parameters with e.s.d.'s*

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

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

The e.s.d.'s given in parentheses refer to the least significant figures in the parameter values. The z coordinate of the sodium atom has been set at zero and fixed.

(*a*) Heavy atoms

All values are × 10^4.

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Na	4511·7 (5)	81·3 (7)	0	33·7 (4)	59·1 (6)	96·9 (12)	−4·8 (4)	0·6 (7)	1·0 (7)
N(1)	2837 (1)	3146 (2)	−1491 (2)	37 (1)	60 (1)	73 (3)	13 (1)	1 (1)	3 (2)
C(1)	3497 (2)	2730 (3)	−2923 (4)	57 (2)	79 (2)	88 (3)	22 (2)	15 (2)	−6 (2)
C(2)	1914 (2)	3842 (2)	−1844 (3)	36 (1)	53 (2)	82 (3)	3 (1)	−5 (2)	2 (2)
O(2)	1699 (1)	4004 (2)	−3380 (2)	61 (1)	106 (2)	80 (3)	27 (1)	−7 (1)	12 (2)
N(3)	1314 (1)	4302 (2)	−581 (2)	32 (1)	61 (2)	88 (3)	12 (1)	−1 (1)	4 (2)
C(4)	1553 (1)	4098 (2)	1071 (3)	31 (1)	48 (2)	86 (3)	−1 (1)	−1 (2)	−1 (2)
O(4)	989 (1)	4552 (1)	2196 (2)	42 (1)	74 (1)	101 (2)	14 (1)	13 (1)	−14 (2)
C(5)	2495 (2)	3312 (2)	1617 (3)	33 (1)	51 (2)	67 (3)	5 (3)	0 (2)	−1 (2)
C(6)	3108 (1)	2789 (2)	125 (3)	32 (1)	48 (1)	79 (4)	3 (1)	−4 (2)	−2 (2)
O(6)	3852 (1)	2080 (1)	343 (2)	46 (1)	79 (1)	116 (3)	29 (1)	−4 (1)	0 (2)
C(7)	3262 (2)	4127 (2)	2678 (3)	37 (1)	67 (2)	98 (4)	3 (1)	−6 (2)	−13 (2)
C(8)	3732 (2)	5208 (2)	1691 (4)	52 (2)	74 (2)	195 (6)	−9 (2)	−8 (3)	1 (3)
C(9)	2100 (2)	2223 (2)	2730 (3)	46 (1)	57 (2)	94 (4)	4 (1)	3 (2)	9 (2)
C(10)	1309 (2)	1397 (2)	1810 (4)	57 (2)	65 (2)	171 (5)	−10 (2)	1 (2)	12 (3)

Table 2 (*cont.*)

(*b*) Hydrogen atoms

Positional parameters are $\times 10^3$.

	x	*y*	*z*	*B*
H(11)	342 (3)	185 (4)	−322 (7)	7·9 (1·0)
H(12)	425 (4)	273 (4)	−265 (7)	6·7 (0·9)
H(13)	347 (4)	329 (4)	−372 (7)	8·2 (1·2)
H(71)	285 (2)	442 (2)	365 (4)	2·9 (0·5)
H(72)	390 (2)	361 (3)	296 (4)	3·5 (0·6)
H(81)	419 (3)	566 (3)	248 (5)	5·3 (0·8)
H(82)	430 (3)	497 (3)	84 (6)	5·8 (0·8)
H(83)	323 (3)	572 (4)	133 (6)	6·1 (0·9)
H(91)	177 (2)	261 (2)	361 (4)	3·2 (0·5)
H(92)	273 (2)	175 (2)	298 (4)	2·8 (0·5)
H(101)	110 (2)	77 (3)	250 (5)	3·8 (0·6)
H(102)	65 (2)	188 (3)	132 (4)	4·1 (0·6)
H(103)	168 (3)	102 (3)	78 (7)	6·7 (1·0)

Table 3. *Intra- and intermolecular distances and angles*

The standard deviations are estimated as follows:

C–N, C–O, C–C bonds within the pyrimidine ring, Na–O and Na–N distances	0·002 Å
C–C bonds in the aliphatic chains	0·003–4
C–H bonds	0·04
C–N–O angles and angles between atoms at the ring	0·3°
C–C–C angles in the diethyl chains	0·5

(*a*) Bond lengths

The values for bond lengths between nonhydrogen atoms are corrected for rigid-body thermal motion. The uncorrected values are given in Fig. 3.

N(1)–C(2)	1·423 Å
C(2)–N(3)	1·344
N(3)–C(4)	1·348
C(4)–C(5)	1·530
C(5)–C(6)	1·514
C(6)–N(1)	1·368
N(1)–C(1)	1·470
C(2)–O(2)	1·246
C(4)–O(4)	1·238
C(6)–O(6)	1·230
C(7)—H(71)	0·97
C(7)—H(72)	1·01
C(8)—H(81)	0·97
C(8)—H(82)	1·02
C(8)—H(83)	0·89
C(9)—H(91)	0·90
C(9)—H(92)	0·96
C(10)–H(101)	0·91
C(10)–H(102)	1·05
C(10)–H(103)	1·01
C(1)—H(11)	0·98
C(1)—H(12)	0·97
C(1)—H(13)	0·87

(*b*) Bond angles (see also Fig. 3).

C(7)–C(5)–C(4)	108·9°
C(9)–C(5)–C(6)	108·4

(*c*) Sodium coordination tetrahedra

O(6)–Na–O(2)*g*	100°
O(6)–Na–O(4)*a*	92
O(6)–Na–N(3)*a*	96
O(6)–Na–C(4)*a*	90
O(6)–Na–O(4′)*i*	104

Table 3 (*cont.*)

(*d*) Close intermolecular approaches

Na——C(4)*a*	2·86 Å
O(2)——H(71)*b*	2·78
O(2)——H(91)*b*	2·79
O(4)——H(11)*d*	2·61
O(6)——H(102)*a*	2·65
N(3)——H(92)*e*	3·1
H(71)—H(103)*d*	2·47
H(71)—H(13)*c*	2·51
H(72)—H(102)*a*	2·61
H(81)—H(12)*f*	2·65
H(82)—H(102)*a*	2·65
H(83)—H(11)*d*	2·45
H(91)—O(2)*c*	2·79
H(92)—H(83)*g*	3·09
H(101)–H(82)*h*	2·74

Symmetry code

	x	*y*	*z*
a	$\frac{1}{2}+x$	$\frac{1}{2}-y$	z
b	x	y	$z-1$
c	x	y	$z+1$
d	$\frac{1}{2}-x$	$\frac{1}{2}+y$	$\frac{1}{2}+z$
e	$\frac{1}{2}-x$	$\frac{1}{2}+y$	$-\frac{1}{2}+z$
f	$1-x$	$1-y$	$\frac{1}{2}+z$
g	$\frac{1}{2}-x$	$-\frac{1}{2}+y$	$\frac{1}{2}+z$
h	$-\frac{1}{2}+x$	$\frac{1}{2}-y$	z
i	$\frac{1}{2}-x$	$-\frac{1}{2}+y$	$-\frac{1}{2}+z$

Discussion

The metharbital ion

The conformation of the metharbital anion (Fig. 1) is similar to that of the barbital anions in sodium barbital (Berking & Craven, 1971) and calcium barbital trihydrate (Berking, 1971*a*), as well as the barbital molecule (Craven, Vizzini & Rodrigues, 1969; Craven & Gartland, 1970). The trioxopyrimidine ring including C(1) is nearly planar and the ethyl groups together with C(5) form a hydrocarbon chain which is nearly in the all *trans* configuration. Deviations from this idealized geometry are given in Table 4(*b*) as atomic displacements from the best least-squares planes and in Table 4(*c*) as torsion angles.

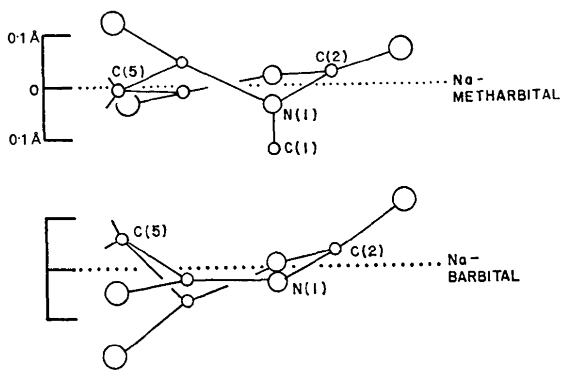


Fig. 2. Conformations of the trioxopyrimidine rings in sodium barbital and sodium metharbital. The dotted lines are the traces of the best least-squares plane through the six ring atoms. The scale in the vertical direction is about six times that in the horizontal.

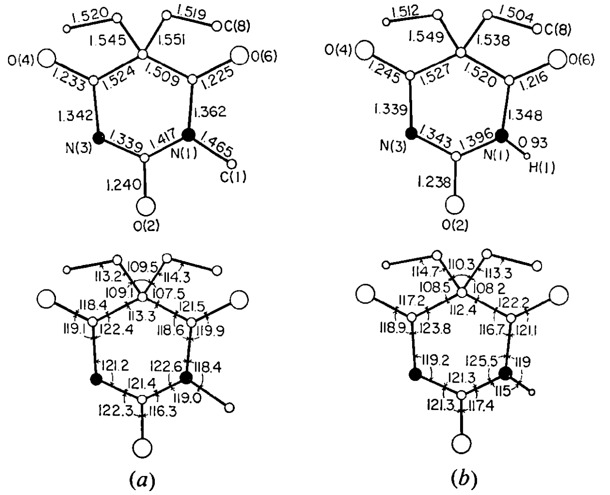


Fig. 3. Bond lengths (Å, top) and bond angles (°, bottom) for (*a*) the metharbital anion and (*b*) the barbital anion in their sodium salts. The e.s.d.'s are given in Table 3.

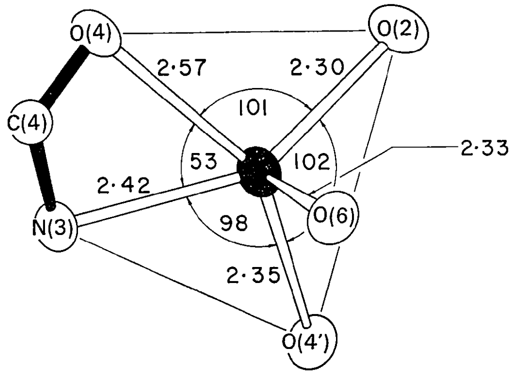


Fig. 4. The coordination of the sodium ion. The atoms N(3)–C(4)=O(4) belong to the same metharbital anion.

The slight puckering of the pyrimidine ring is shown in Fig. 2. It is evident that atoms N(1) and C(6) are farthest out of the plane, with a twist of 9·2° along N(1)–C(6), whereas in the barbital anion of sodium barbital and in three of four independent ions in calcium barbital trihydrate (the fourth one being flat) the tetrahedrally surrounded atom C(5) is farthest out of the plane, probably in order to relieve angular strain induced by the ring closure. All torsion angles including hydrogen atoms within the ethyl groups show *anti* conformation.

Bond lengths and bond angles for the metharbital ion are shown in Fig. 3 and Table 3 and if relevant are compared with those of the barbital anion in sodium barbital. As expected, these are very similar for the C–C bonds in the aliphatic chains and differ from the expected value (1·526 Å, Lide, 1962) in the same way: C(5)–C(7) and C(5)–C(9) are elongated, probably because of steric hindrance around C(5), whereas the terminal bonds C(7)–C(8) and C(9)–C(10) are shortened, probably because of high thermal motion. Within the trioxypyrimidine ring, the C–N and C–O bonds show the characteristic features of deprotonation (Singh, 1965): the internal angle at N(3) is reduced by 5°. The C–N bonds on the deprotonation site N(3) are shorter (1·339 and 1·342 Å) than those at the nondeprotona-

Table 4. *Least-squares planes and torsion angles*

Plane 1: Through the six pyrimidine ring atoms.
Plane 2: Through C(2), N(3), C(4), C(5).
Plane 3: Through the atoms of the chain C(5), C(7), C(8), C(9), C(10).
Plane 4: Through the atoms of the base of the coordination pyramid.

(*a*) Equations of the planes

$$\begin{aligned}
&\text{Plane 1:} && 0·571x+0·820y+0·028z= 4·762\\
&\text{Plane 2:} && 0·571x+0·821y+0·016z= 4·762\\
&\text{Plane 3:} && 0·760x-0·570y-0·312z=-0·029\\
&\text{Plane 4:} && -0·417x+0·908y+0·043z=-2·658
\end{aligned}$$

(*b*) Distances (Å) of atoms from the least-squares planes. The underlined values belong to atoms forming the planes. The e.s.d.'s are 0·002 Å for planes (1), (2), and (4) and 0·003–0·004 Å for plane (3).

	Plane 2	Plane 2	Plane 3
N(1)	0·044	0·058	–
C(2)	−0·015	0·003	–
N(3)	−0·014	−0·007	–
C(4)	0·015	0·006	−1·256
C(5)	0·011	−0·003	0·001
C(6)	−0·040	−0·041	1·277
C(1)	0·121	0·148	–
O(2)	−0·061	−0·028	–
O(4)	0·033	0·014	–
O(6)	−0·126	−0·129	–
C(7)	1·312	1·288	−0·020
C(8)	2·587	2·573	0·009
C(9)	−1·214	−1·239	0·019
C(10)	−2·537	−2·554	−0·010

Plane 4:	O(2)*g*	O(4')*i*	N(3)*a*	O(4)*a*	Na	O(6)	C(4)*a*
	−0.006	0.007	−0.011	0.010	0.356	2.676	0.119

(*c*) Torsion angles within the pyrimidine ring (e.s.d.'s, 0·2°)

Bond vector	Torsion angle
N(1)–C(2)	7·23°
C(2)–N(3)	−1·43
N(3)–C(4)	−1·59
C(4)–C(5)	−0·55
C(5)–C(6)	5·79
C(6)–N(1)	−9·24

Torsion angles, including atoms of the methyl and the ethyl groups (e.s.d.'s, 0·3–0·4°)

C(1)–N(1)–C(2)–N(3)	−176·32°
C(1)–N(1)–C(2)–O(2)	3·35
C(1)–N(1)–C(6)–C(5)	174·29
C(1)–N(1)–C(6)–O(6)	−4·14
C(9)–C(5)–C(7)–C(8)	178·02
C(7)–C(5)–C(9)–C(10)	177·90
N(3)–C(4)–C(5)–C(7)	119·03
N(3)–C(4)–C(5)–C(9)	−121·46
N(1)–C(6)–C(5)–C(7)	−114·57
N(1)–C(6)–C(5)–C(9)	127·07

Table 4 (*cont.*)

Torsion angles including hydrogen atoms:

H(71)-C(7)-C(8)—H(81)	60°	H(92)-C(9)-C(10)-H(101)	64°
H(82)	167	H(102)	−171
H(83)	−58	H(103)	−54
H(72)-C(7)-C(8)—H(81)	−64	C(2)—N(1)-C(1)—H(11)	−104
H(82)	42	H(12)	145
H(83)	178	H(13)	34
H(91)-C(9)-C(10)-H(101)	−67	C(6)—N(1)-C(1)—H(11)	73
H(102)	58	H(12)	−38
H(103)	176	H(13)	−150

* Symmetry code: see Table 3.

tion site (1·362 and 1·417 Å); the two C–O bonds adjacent to N(3) are longer (1·240, 1·233 Å) than the remote C–O bond (1·225 Å) in this compound and the corresponding values in the crystal structure of the free acid metharbital (1·205, 1·209, 1·221 Å, Wunderlich, 1971). This indicates that part of the formal negative charge of the anion is equally distributed between the O(2) and O(4) oxygen atoms.

Methylation of the trioxopyrimidine ring at N(1) has the effect of decreasing the internal angle at N(1) (122·6 *vs.* 125·5° in sodium barbital) and lengthening the two adjacent C–N bonds (1·417 and 1·362 Å *vs.* 1·396 and 1·348 Å); other parts of the ring do not seem to be affected if the compensation for the decrease in the angle C(6)–N(1)–C(2) is neglected. The C–O bonds are shorter (Fig. 3) than most of the corresponding ones in the barbital anions of the sodium and calcium salt and longer than those in the metharbital acid. Obviously, these results cannot be attributed to the decreasing degree of participation in hydrogen-bonding within these groups. Rather, they suggest that *N*-methylation and differences in interactions with the sodium ion may also be important. All C–H distances (average 0·97 Å) are in expected ranges.

The coordination of the sodium ion and the crystal packing

The crystal packing is dominated by ionic interactions. The sodium ion is fivefold coordinated (Fig. 4): three metharbital oxygen atoms and the deprotonated nitrogen atom form the base, and another oxygen atom, O(6), forms the apex of a pyramid surrounding the sodium ion. The coordination polyhedron may also be pictured as a tetrahedron, in which one corner is replaced by the intramolecular grouping N(3)–C(4)=O(4). Of particular interest is the coordination of the sodium ion by a nitrogen atom, the Na–N distance 2·42 Å being the shortest one so far reported. While three Na–O distances are in the expected range (2·30–2·35 Å), the fourth involving atom O(4), which is part of the same metharbital ion as N(3), is extremely long (2·57 Å). O(4) is the only oxygen atom that simultaneously coordinates two Na atoms.

The alkaline and alkaline-earth metal ions are known to prefer coordination by oxygen rather than by nitrogen. In the few reported cases of coordination of the sodium ion by nitrogen, the Na–N distances are at least 2·50 Å, even in the structures of sodium azide NaN_3 (Pringle & Noakes, 1968; Hendricks & Pauling, 1925) and $NaCl.5\frac{1}{7}NH_3$ (Olovsson, 1965) where there are no competing oxygen atoms. Only in different modifications at low temperatures do these structures show Na–N distances of 2·44 and 2·47Å, which are comparably short.

In the crystal structures of salts of barbiturates where cation coordination by deprotonated nitrogen atoms *a priori* could be possible, three different degrees of involvement of the N atom in the coordination have been found: in sodium barbital (Berking & Craven, 1971), and in the isomorphous potassium barbital (Berthou, Rérat & Rérat, 1965), the cation is surrounded by an almost regular tetrahedron consisting of barbital oxygen atoms. In sodium barbital, all four Na–O distances are within 2·31–2·35 Å, whereas the deprotonated nitrogen atom N(3) with Na–N = 2·80 Å is not involved in intermolecular interactions at all.

In the crystal structure of calcium barbital trihydrate (Berking, 1971*a*,*b*), the coordination may be pictured as an octahedron in which one corner is replaced by the same intramolecular grouping, namely N(3)–

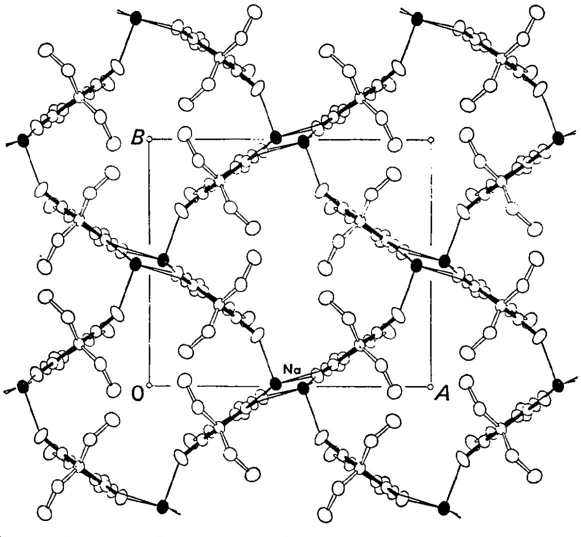


Fig. 5. The crystal structure of sodium metharbital as a projection down the *c* axis.

C(2)=O(2). Here, the Ca–N distances (2·52 and 2·55 Å for two independent Ca ions) are only 0·08 and 0·04 Å shorter than the Ca–O(2) distances (2·60 and 2·59 Å). This may not give sufficient evidence that the Ca–N interaction is primarily due to the coordination need of the Ca ion and the electronegativity of the deprotonated nitrogen, but it still allows the assumption that it is a consequence of the rigid N–C=O grouping, where the coordination itself is by the O atoms.

Finally, in the structure of sodium metharbital reported here, the relatively large difference of 0·15 Å between the short Na–N distance and the long Na–O(4) distance clearly indicates that N(3) does coordinate the Na ion, and that it is, at least, not much less electronegative than the competing oxygen atoms at the pyrimidine ring. There is no evidence that the involvement of N(3) in the cation coordination affects the intramolecular N(3)–C bonds (1·339 and 1·342 Å in sodium metharbital *vs.* 1·339 and 1·343 Å in sodium barbital).

Intermolecular interactions other than ionic are less important. Van der Waals interactions are weak, the shortest H···H intermolecular distance is 2·45 Å and there are seven additional distances less than 2·70 Å [Table 3(*d*)]. For an H···H approach, $d=2{\cdot}4$ Å could be expected (Pauling, 1960). The shortest intermolecular C–O distance is 3·70 Å, indicating that there are no C=O···C=O dipole–dipole interactions.

The packing of the molecules in the unit cell (Figs. 5 and 6) is similar to that in the crystal structure of sodium barbital (Fig. 3 in Berking & Craven, 1971), with respect to the hydrophobic and hydrophilic channels along the shortest axis and the orientation of the trioxopyrimidine ring. This is consistent with a certain similarity in lattice dimensions. Despite these agreements, hydrogen-bonding in sodium barbital seems to be a dominant factor.

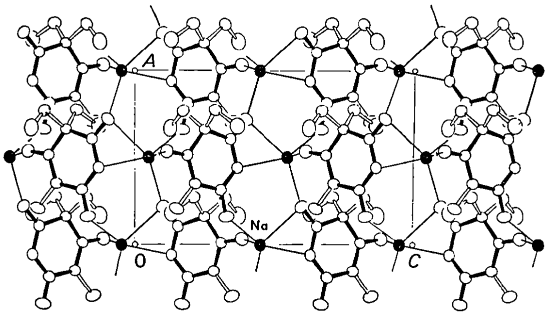


Fig. 6. The crystal structure of sodium metharbital as a projection along the *b* axis.

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