Acta Cryst. (1964). **17**, 282

The Crystal Structure of Ammonium Barbiturate

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(*Received* 18 *April* 1963)

Ammonium barbiturate ($NH_4C_4H_3O_3N_2$) is monoclinic, space group $P2_1/n$ with cell parameters $a = 10{\cdot}709$, $b = 3{\cdot}8519$, $c = 14{\cdot}345$ Å and $\beta = 95° \tfrac{1}{2}'$ and with four formula units in the unit cell. An X-ray crystal structure analysis has been carried out with three-dimensional data which were obtained partly by photographic and partly by counter methods. The structure parameters, which were refined by full-matrix least-squares methods, were the atomic positional and isotropic thermal parameters together with individual scaling factors for the layers $k = 0$ through 4. The hydrogen atom positions were obtained from a difference Fourier map. Bond lengths and bond angles were determined with e.s.d.'s of 0·01 Å and 0·8° respectively. The molecular packing features a three-dimensional network of hydrogen bonds.

Introduction

The purpose of this analysis was to study the structure of the barbiturate ion in the crystalline state and to compare its structure with that of the parent acid as determined in previous crystal structure analyses of barbituric acid (Bolton, 1963) and barbituric acid dihydrate (Jeffrey, Ghose & Warwicker, 1961). The ammonium salt was chosen since it was anticipated that this would have a crystal structure in which the mode of molecular packing and the nature of the hydrogen bonding would be of considerable interest.

Experimental

Pale orange crystals of ammonium barbiturate were obtained by slow evaporation of an aqueous solution at room temperature. They were invariably in clusters of very thin monoclinic plates, elongated along *b*, with {101} the predominant form. It was difficult to isolate suitable single crystals because they were very hard and brittle, fracturing without cleavage.

The X-ray data were all collected from one crystal which was approximately 0·3 × 0·02 × 0·1 mm in dimensions. The cell data listed in Table 1 were obtained with a G. E. XRD 5 diffractometer and single-crystal orienter with an aged X-ray tube which conveniently emitted both Cu *K* and Fe *K* radiation. Intensity data for the reciprocal lattice layers $k = 0, 1, 2$ and 3 and $l = 0$ and 1 were recorded on multifilms, the equi-inclination Weissenberg technique being used with Cu $K\alpha$ radiation, and were estimated by eye against a standard scale. No X-ray absorption corrections were applied. Data reduction was affected by a series of FORTRAN programs for the IBM 7070 computer (Craven, unpublished) which incorporated interlayer scaling by a least-squares procedure similar to that described by Rollett & Sparks (1960). At a later stage of the analysis, the intensities of 93 reflexions in the layer $k = 4$ were recorded on the XRD 5 diffractometer, since the equi-inclination angle for this layer was not accessible to the Weissenberg camera. As described below, the scaling factors for the layers $k = 0$ through 4 were later adjusted as structure parameters because of the insufficient data available for reliable experimental correlation of these layers.

Table 1. *The crystal data*

Ammonium barbiturate $NH_4C_4H_3O_3N_2$ M.W. 145·1

Monoclinic

$a = 10{\cdot}709 \pm 0{\cdot}001$ Å	$U = 588{\cdot}5$ Å^3
$b = 3{\cdot}8519 \pm 0{\cdot}005$	$D_x = 1{\cdot}64$ g.cm^{-3}
$c = 14{\cdot}345 \pm 0{\cdot}001$	$D_m = 1{\cdot}67$ g.cm^{-3}
$\beta = 95° \tfrac{1}{2}' \pm 1'$	$Z = 4$

Space group: $P2_1/n$

A total of 1202 non-symmetry-related reflexions *hkl* were examined, of which 126 were too weak to be observed and were assumed to have one half of the minimum observable intensity.

The structure determination

The peaks immediately surrounding the origin in the Patterson function $P(uw)$ clearly revealed the orientation of the barbiturate ion as one of three symmetry-related possibilities. These arise from the carbon, nitrogen and oxygen atoms being of comparable X-ray scattering power so that the ion has a pseudo point symmetry of $\bar{6}m$. The true molecular orientation and also the ammonium nitrogen atom position were deduced from packing considerations and the requirements of hydrogen bonding. The projection down *c*, in which the barbiturate ion appears almost edge on, was then considered in order to derive approximate atomic *y* parameters.

After Fourier refinement had reduced the usual *R* index to 0·20 for the *h*0*l* and 0*kl* structure factors, the refinement was continued in three dimensions, using all except the *h*4*l* data which were not then

Table 2: *The observed and calculated structure factors*

The columns are successively, h, l, $100 \times |F(\text{obs.})|$ and $100 \times F(\text{calc.})$. Reflexions marked * are either those which were unobserved or those which were omitted from the least-squares refinement since they were considered to be affected by X-ray extinction

k = 0

2	0	3599	4766-*
4	0	718	640-
6	0	1006	999-
8	0	1589	1741
10	0	848	941-
12	0	200	172-
1	1	3740	4570 *
1-	1		217 *
3	1	3010	2416 *
3-	1	128	40-*
5	1	3747	3028-*
5-	1	3377	3163 *
7	1	2674	2174
7-	1	665	630-
9	1	809	859
9-	1	1103	1062
11	1	882	953
11-	1	3230	3818-
13	1	449	525-
13-	1	184	70 *
0	2	2223	2298 *
2	2	3271	3595-*
2-	2	4457	4504-*
4	2	928	778
4-	2	2117	2136-
6	2	4647	4839 *
6-	2	599	659-
8	2	1446	1064
8-	2	1100	1211
10	2	282	106
10-	2	2664	2957-
12	2	233	207
12-	2	973	847
1	3	2940	3649 *
3	3	3253	2923 *
3-	3	6314	7834-*
5	3	4409	4032-*
5-	3	3340	2942-
7	3	3285	3609
7-	3	1565	1574-
9	3	282	393-
9-	3	1684	1699
11	3	741	781
11-	3	1559	1574-
13	3	406	354-
0	4	3107	3142-*
2	4	2984	3103 *
2-	4	1363	1448
4	4	2589	2482-
4-	4	6337	6089-*
6	4	2188	1966-
6-	4	3296	3048
8	4	774	610-
8-	4	701	538-
10	4	278	22-
10-	4	2174	2622-
12	4	2188	1824
12-	4	856	736
1	5	6901	7507-*
1-	5	1405	770-
3	5	3153	3355-*
5	5	223	160
5-	5	2860	2758
7	5	263	392-
9	5	283	5-
9-	5	1379	1127-
11	5	245	429-
11-	5	1027	971
0	6	2536	2338
2	6	3631	4129-*
2-	6	1523	1263-
4	6	1120	980-
4-	6	2214	2016-
6	6	254	344
6-	6	1623	1723
8	6	282	317
8-	6	1487	1382
10	6	1677	1835-
10-	6	1572	1447
12	6	181	60 *
1	7	1359	1067
1-	7	1577	1282
3	7	1644	1573
3-	7	580	358-
5	7	248	80
5-	7	1815	1535
7	7	1778	1850-
7-	7	996	570
9	7	996	940-
9-	7	283	485
11	7	915	914-
11-	7	251	109
13-	7	728	701
0	8	4736	4708
2	8	3158	3551-
2-	8	1935	2042
4	8	247	17-
4-	8	3692	3587
6	8	2445	2637
6-	8	737	581-
8	8	1639	1800-
8-	8	489	479-
10	8	827	966-
10-	8	268	375-
1	9	232	45
1-	9	2888	2694
3	9	249	39
3-	9	1010	1182
5	9	1637	1574-
5-	9	259	330-
7	9	3513	4084
7-	9	626	644-
9	9	254	286-
9-	9	2066	2193
11-	9	1788	1691-
0	10	779	470
2	10	1704	1626
2-	10	930	1027
4	10	273	41-
4-	10	4011	4398-
6	10	2784	2851
6-	10	1445	1108
8	10	263	728-
8-	10	794	789
10-	10	1172	975-
1	11	266	262
1-	11	694	321
3	11	276	271
3-	11	968	297-
5	11	1020	734-
5-	11	1340	1309-
7	11	2276	2219
7-	11	1759	1716-
9	11	786	759-
0	12	781	428-
2-	12	2887	3092
4	12	1871	1968-
4-	12	4216	4808-
6	12	268	255
6-	12	1162	971
8	12	694	794
1	13	1202	1144
1-	13	1858	1619-
3	13	1791	1921-
3-	13	2414	2312-
5	13	266	75
5-	13	280	459
7	13	446	504-
7-	13	1636	1768
0	14	281	183-
2	14	1034	702-
2-	14	795	586-
4	14	260	329
4-	14	276	583-
6-	14	258	200
8-	14	1121	917
1	15	1300	1594
1-	15	539	420
3	15	1527	1660-
3-	15	265	231
5-	15	248	252-
7-	15	1015	785
2-	16	246	409-
4-	16	1605	1222
6-	16	200	419
3-	17	1423	1123

k = 1

2	0	5529	7680 *
3	0	1835	2049-
4	0	1471	1459-
5	0	1457	1292
6	0	1001	943-
7	0	1427	1677
8	0	207	208-
9	0	218	239
10	0	817	1027
11	0	206	91
12	0	178	324-
13	0	973	1057-
1	1	1574	1812
1-	1	1406	4086-*
2	1	8347	11713 *
2-	1	1831	1712
3	1	2387	2356
3-	1	1832	1757
4	1	2075	1971
4-	1	2341	2646-
5	1	1537	1317-
5-	1	488	511
6	1	755	683
6-	1	721	780
7	1	278	301-
7-	1	223	276
8	1	245	77-
8-	1	989	1082-
9	1	361	311-
9-	1	1575	1645-
10	1	596	587
10-	1	607	644
11	1	703	772
11-	1	242	217-
12	1	537	553-
12-	1	907	1658-
13	1	152	149-*
13-	1	1134	1302
0	2	2772	2752-
1	2	2997	2704
1-	2		2193 *
2	2	3649	3354 *
2-	2	404	260-
3	2	2286	2064-
3-	2	1866	1910
4	2	2169	1968-
4-	2	392	317
5	2	4142	4096
5-	2	3148	3579-
6	2	1325	1077-
6-	2	1245	1469
7	2	1300	1425-
7-	2	197	0-
8	2	1025	1322
8-	2	960	965-
9	2	1123	1235
9-	2	3206	3528-
10	2	391	244-
10-	2	683	688-
11	2	209	89-
11-	2	859	975
12	2	178	265
12-	2	837	1073
13	2	797	923
13-	2	143	203-*
0	3	509	321
1	3	1638	1344-
1-	3	2610	2419-
2	3	2409	2115-
2-	3	2900	3076-
3	3	3234	2838
3-	3	1573	1512-
4	3	2012	1869-
4-	3	711	681
5	3	1051	1011-
5-	3	1430	1465
6	3	681	596-
6-	3	1750	1814-
7	3	1151	1078-
7-	3	1244	1506
8	3	1872	2050
8-	3	717	703-
9	3	758	780
9-	3	1627	1573-
10	3	1255	1401
10-	3	643	562
11	3	354	270-
11-	3	675	625
12	3	170	289
12-	3	1382	1480-
13-	3	373	309
0	4	114	1 *
1	4	2417	1988-
1-	4	5274	6519-*
2	4	344	468-
2-	4	2134	2240-
3	4	408	367
3-	4	2589	2547-
4	4	1686	1743
4-	4	1394	1153
5	4	1019	813
5-	4	1001	1032-
6	4	732	810-
6-	4	972	1154
7	4	972	948-
7-	4	1942	2066
8	4	224	339
8-	4	2054	2290-
9	4	457	551
9-	4	852	838-
10	4	730	987-
10-	4	750	567
11	4	342	456
11-	4	211	91-
12	4	161	179-*
12-	4	1122	1144
13-	4	576	500
0	5	1875	1580-
1	5	995	680
1-	5	2127	2118
2	5	2165	2023-
2-	5	2358	2456-
3	5	1597	1776-
3-	5	511	442
4	5	1014	991
4-	5	2076	1875
5	5	561	333
5-	5	768	685
6	5	575	461-
6-	5	1671	1797-
7	5	576	416-
7-	5	1352	1361-
8	5	1436	1663-
8-	5	701	468-
9	5	850	828
9-	5	228	35
10	5	304	236-
10-	5	809	891
11	5	654	765-
11-	5	622	537
12	5	331	333-
12-	5	1351	1513
13-	5	128	58 *
0	6	2463	2455
1	6	448	554
1-	6	2241	1935
2	6	498	251
2-	6	2802	3027-
3	6	2410	2379-
3-	6	1384	1309
4	6	1083	1171-
4-	6	2090	2075
5	6	2761	2715-
5-	6	185	44
6	6	211	148
6-	6	490	362
7	6	546	286-
7-	6	214	11-
8	6	605	571
8-	6	225	14-
9	6	897	1064-
9-	6	1009	958
10	6	207	125
10-	6	222	56-
11	6	177	195
11-	6	202	64
12	6	320	567-
12-	6	169	80
13-	6	514	528
0	7	3417	3274-
1	7	995	738
1-	7	1384	1210-
2	7	1681	1547
2-	7	1915	1903
3	7	603	355-
3-	7	668	476
4	7	643	406-
4-	7	1283	1570
5	7	207	61-
5-	7	195	87
6	7	1218	1269-
6-	7	2381	2574
7	7	936	902
7-	7	220	358-
8	7	603	387-
8-	7	820	710
9	7	218	110-
9-	7	394	460
10	7	482	492
10-	7	217	247-
11	7	162	266-*
11-	7	194	301-
12-	7	159	167 *
0	8	1687	1509
1	8	849	638
1-	8	176	151
2	8	1508	1382
2-	8	507	271-
3	8	872	690-
3-	8	1850	1771
4	8	2118	2436-
4-	8	1015	1006-
5	8	3090	3428
5-	8	882	674
6	8	674	573
6-	8	778	754-
7	8	229	257-
7-	8	225	550
8	8	1165	1193
8-	8	229	382
9	8	755	879-
9-	8	502	377-
10	8	549	541-
10-	8	364	318-
11	8	701	737-
11-	8	1299	1214
12-	8	632	626
0	9	1458	1591
1	9	1159	1174
1-	9	191	287
2	9	1999	2095
2-	9	1931	1896
3	9	881	834
3-	9	990	845-
4	9	748	567
4-	9	206	88
5	9	2148	2410-
5-	9	215	377-
6	9	823	734-
6-	9	1727	1815-
7	9	717	593
7-	9	1123	1102
8	9	1236	1516
8-	9	228	83-
9	9	709	867
9-	9	693	494-
10	9	720	931-
10-	9	602	573
11-	9	594	594-
12-	9	400	339-
0	10	290	201-
1	10	1786	1460
1-	10	579	647
2	10	902	749
2-	10	988	924-
3	10	977	672-
3-	10	298	30
4	10	744	543-
4-	10	719	720-
5	10	1689	1818
5-	10	771	668-
6	10	720	635-
6-	10	1971	2065
7	10	1265	1431-
7-	10	1022	929
8	10	819	1162
8-	10	836	531-
9	10	1074	1226
9-	10	1901	1978-
10-	10	595	605-
11-	10	380	330-
0	11	217	66
1	11	380	295
1-	11	376	256
2	11	1350	1279-
2-	11	2473	2830-
3	11	452	380
3-	11	1716	1594-
4	11	1114	957
4-	11	2300	2664
5	11	939	857-
5-	11	394	410
6	11	314	344
6-	11	2012	1952-
7	11	209	181-
7-	11	225	366
8	11	1778	1796
8-	11	216	143-
9	11	1085	1081
9-	11	198	182-
10-	11	172	177-
11-	11	133	110 *
0	12	1315	1381
1	12	1130	1149-
1-	12	713	572
2	12	823	715
2-	12	2172	2051-
3	12	229	245
3-	12	1597	1565-
4	12	227	223-
4-	12	228	193-
5	12	221	48-
5-	12	2061	2076-
6	12	786	984-
6-	12	1390	1417
7	12	333	398
7-	12	217	112
8	12	166	29 *
8-	12	673	586-
9	12	127	355 *
9-	12	726	744
10-	12	427	406-
0	13	758	823
1	13	646	507
1-	13	1072	1087-
2	13	227	139
2-	13	2340	2437-
3	13	224	201
3-	13	228	7-
4	13	488	612-
4-	13	507	469
5	13	208	83-
5-	13	1513	1608
6	13	1286	1146-
6-	13	482	479-
7	13	654	634-
7-	13	407	300-
8-	13	186	58-
9-	13	599	466-
10-	13	121	227-*
0	14	224	73
1	14	1909	2009-
1-	14	224	174
2	14	309	283
2-	14	894	851-
3	14	424	462
3-	14	313	442
4	14	452	582-
4-	14	870	787
5	14	1422	1321-
5-	14	942	889
6	14	668	701
6-	14	283	330
7	14	138	119 *
7-	14	184	277-
8-	14	163	90-*
9-	14	613	629
0	15	557	334-
1	15	548	499
1-	15	872	797-
2	15	201	176-
2-	15	210	327
3	15	769	681
3-	15	207	196
4	15	536	416-
4-	15	284	263-
5	15	554	512-
5-	15	192	61
6	15	133	266-*
6-	15	1443	1236
7-	15	159	126 *
8-	15	131	211 *
0	16	597	470-
1	16	714	578
1-	16	190	215
2	16	176	435
2-	16	189	381
3	16	805	872
3-	16	185	485-
4	16	147	232-*
4-	16	177	67-
5-	16	843	702
6-	16	727	494
0	17	159	29-*
1	17	610	506-

Table 2 (*cont.*)

k = 1

1-	17	557	442
2	17	749	638
2-	17	713	710
3	17	124	46-*
3-	17	154	211 *
4-	17	1086	814
5-	17	128	69-*
0	18	113	534 *
1-	18	838	840

k = 2

1	0	570	771
2	0	218	129-
3	0	1071	1402
4	0	2280	2843
5	0	1282	1333-
6	0	1253	1285-
7	0	552	588-
8	0	269	116-
9	0	740	841
10	0	692	844-
11	0	457	519
0	1	1437	1928-
1	1	2405	2837-
1-	1	392	284
2	1	2627	2854-
2-	1	408	300-
3	1	4396	5493 *
3-	1	2379	2598
4	1	2366	3052
4-	1	613	558
5	1	1197	1258-
5-	1	1148	1387
6	1	482	443
6-	1	460	518
7	1	892	955
7-	1	1543	1844-
8	1	655	603-
8-	1	354	299-
9	1	238	98
9-	1	354	284-
10	1	311	265
10-	1	315	136-
11	1	610	728
11-	1	574	622-
12	1	120	317
12-	1	125	205-
0	2	1213	1154-
1	2	980	744
1-	2	310	205
2	2	2968	3056-
2-	2	302	267
3	2	776	520-
3-	2	1735	1711-
4	2	3993	4498
4-	2	225	74-
5	2	151	80
5-	2	389	268-
6	2	1020	949
6-	2	564	561-
7	2	254	351
7-	2	1506	1268-
8	2	673	785
8-	2	1161	1288-
9	2	524	412-
9-	2	996	940
10	2	347	329
10-	2	397	256-
11	2	336	189-
11-	2	498	497
12	2	114	95 *
12-	2	864	887
0	3	333	161
1	3	1442	1325-
1-	3	425	256
2	3	367	187
2-	3	106	95-*
3	3	1555	1466
3-	3	2453	2901-
4	3	488	377
4-	3	270	310
5	3	156	127
5-	3	398	456
6	3	997	752-
6-	3	619	514-
7	3	603	603
7-	3	2991	4131-
8	3	1425	1819-
8-	3	322	433
9	3	184	93
9-	3	1698	1780
10	3	588	953
10-	3	585	574-
11	3	355	436
11-	3	412	303
12	3	104	514 *
12-	3	302	235-
0	4	2090	2169-
1	4	2059	1969-
1-	4	1188	1061-
2	4	300	45-
2-	4	117	30-
3	4	556	354-
3-	4	2180	2176
4	4	900	893-
4-	4	1077	882-
5	4	514	409
5-	4	1586	1791
6	4	793	821-
6-	4	960	935-
7	4	943	936
7-	4	1102	1003-
8	4	722	750-
8-	4	619	676-
9	4	1111	1512-
9-	4	185	157-
10	4	679	963
10-	4	302	294
11	4	336	406
11-	4	342	179
12-	4	119	106-
0	5	1649	1594-
1	5	1640	1581-
1-	5	2066	1972-
2	5	520	610-
2-	5	2781	3163
3	5	2253	2541-
3-	5	1277	1146
4	5	472	538-
4-	5	1484	1340-
5	5	169	93-
5-	5	842	670
6	5	1133	1386
6-	5	863	787-
7	5	618	771-
7-	5	976	933-
8	5	186	190-
8-	5	1055	1066
9	5	354	294
9-	5	897	850
10	5	223	201-
10-	5	980	846
11	5	568	552
11-	5	663	555
12-	5	112	138-*
0	6	1191	984-
1	6	1309	1285
1-	6	802	517
2	6	527	481
2-	6	487	461-
3	6	1013	759
3-	6	906	858-
4	6	1374	1548-
4-	6	650	541
5	6	394	422-
5-	6	933	716-
6	6	368	331-
6-	6	666	331-
7	6	459	172
7-	6	614	385
8	6	183	159
8-	6	1610	1678
9	6	591	548-
9-	6	181	117-
10	6	629	572-
10-	6	1081	1063
11	6	253	342-
11-	6	777	591
0	7	1027	902-
1	7	589	410
1-	7	149	56-
2	7	821	816-
2-	7	2837	3057
3	7	2375	2893
3-	7	957	948
4	7	832	954
4-	7	166	44-
5	7	1720	1879-
5-	7	175	29
6	7	187	66
6-	7	365	282-
7	7	1087	1234-
7-	7	1183	1193
8	7	178	357-
8-	7	821	863-
9	7	281	112-
9-	7	177	58
10	7	136	39
10-	7	160	273
11	7	92	22-*
11-	7	565	472
0	8	1336	1252
1	8	232	210
1-	8	1361	1204
2	8	413	282
2-	8	714	733
3	8	1887	2119-
3-	8	169	61-
4	8	601	663
4-	8	1785	1669
5	8	644	596
5-	8	543	430-
6	8	794	828-
6-	8	951	929
7	8	730	847
7-	8	187	68
8	8	483	474-
8-	8	848	789-
9	8	739	741
9-	8	343	226
10	8	120	117
10-	8	152	125-
11-	8	609	471
0	9	572	503
1	9	1106	939-
1-	9	998	781
2	9	178	191
2-	9	1199	1126-
3	9	2580	3010
3-	9	177	86
4	9	526	588
4-	9	1068	951-
5	9	1338	1547-
5-	9	1281	1490
6	9	319	412-
6-	9	495	412-
7	9	745	799
7-	9	932	798-
8	9	160	9
8-	9	1053	1117
9	9	788	815
9-	9	565	427
10-	9	141	320
11-	9	546	584-
0	10	572	498-
1	10	965	813
1-	10	829	653-
2	10	1133	1167
2-	10	575	443-
3	10	673	405-
3-	10	184	177-
4	10	1583	1874
4-	10	1086	1068-
5	10	523	565
5-	10	187	65-
6	10	590	483
6-	10	1179	1354
7	10	437	285-
7-	10	651	371-
8	10	1093	1089-
8-	10	1292	1489-
9	10	569	557-
9-	10	481	366-
10-	10	126	76
0	11	186	166-
1	11	528	486
1-	11	1427	1569-
2	11	495	301-
2-	11	996	909
3	11	1031	1006
3-	11	187	124
4	11	689	736-
4-	11	187	351
5	11	308	337
5-	11	950	961
6	11	473	225-
6-	11	1065	1083-
7	11	150	138-
7-	11	2314	2751-
8	11	126	11
8-	11	708	684
9-	11	138	73-
10-	11	106	180-*
0	12	1793	2128-
1	12	372	356
1-	12	748	772-
2	12	185	212
2-	12	1093	1158
3	12	182	5
3-	12	616	591-
4	12	609	580-
4-	12	757	635-
5	12	470	456-
5-	12	179	247
6	12	152	306
6-	12	344	197-
7	12	131	73
7-	12	1351	1279
8-	12	1106	939-
0	13	1319	1512-
1	13	476	247
1-	13	2172	2597-
2	13	585	541
2-	13	512	288
3	13	1021	971-
3-	13	693	600
4	13	1112	1181
4-	13	303	247
5	13	516	424
5-	13	168	148
6	13	413	408-
6-	13	158	89
7-	13	144	9
8-	13	123	67-
0	14	1608	1780-
1	14	167	77-
1-	14	837	795
2	14	162	306
2-	14	635	563
3	14	154	305-
3-	14	372	288
4	14	143	3-
4-	14	360	308
5	14	519	434
5-	14	152	120-
0	15	152	59-
1	15	148	35-
1-	15	531	469
2	15	142	240-
2-	15	263	162
3	15	131	223-
3-	15	1043	924
4	15	541	577
4-	15	599	568
5-	15	505	418-
0	16	583	509
2-	16	127	150
3-	16	212	114
4-	16	884	880

k = 3

1	0	816	873
2	0	734	888
3	0	606	478-
4	0	896	956
5	0	1724	2151
6	0	177	102
7	0	343	246-
8	0	168	8
9	0	260	286-
10	0	590	460-
0	1	694	581-
1	1	1451	1819-
1-	1	1308	1561
2	1	2094	2158
2-	1	865	881
3	1	681	597-
3-	1	830	759
4	1	332	256-
4-	1	208	61
5	1	1340	1769
5-	1	1089	1126-
6	1	1677	2113
6-	1	541	483-
7	1	846	938-
7-	1	799	977-
8	1	524	515-
8-	1	619	700-
9	1	675	494-
9-	1	361	73-
10	1	154	76-
10-	1	598	411
11	1	141	114
0	2	739	831
1	2	1108	1242
1-	2	443	534-
2	2	1482	1574-
2-	2	797	642
3	2	1221	1256-
3-	2	1092	1041
4	2	1746	1852-
4-	2	265	101-
5	2	1522	1934
5-	2	1822	2064-
6	2	665	723
6-	2	856	741-
7	2	119	33-*
7-	2	395	330
8	2	538	663
8-	2	116	98 *
9	2	347	313
9-	2	1251	1351-
10	2	87	114 *
10-	2	680	756
0	3	383	233-
1	3	78	25 *
1-	3	984	1057-
2	3	547	534-
2-	3	511	489-
3	3	638	693-
3-	3	373	151-
4	3	1115	1242-
4-	3	253	190-
5	3	991	1170
5-	3	1221	1071-
6	3	1087	1429
6-	3	1174	1175-
7	3	871	1035-
7-	3	1337	1544
8	3	620	659
8-	3	259	206-
9	3	287	373
9-	3	907	1015
10	3	368	435-
10-	3	91	140-*
0	4	85	48-*
1	4	1206	1380-
1-	4	496	506-
2	4	95	34-*
2-	4	635	500-
3	4	536	559-
3-	4	99	54 *
4	4	399	392
4-	4	786	731
5	4	599	621-
5-	4	2117	2365-
6	4	652	407
6-	4	1064	832-
7	4	1121	1094
7-	4	1293	1256
8	4	788	564-
8-	4	303	222
9	4	292	302
9-	4	105	201-*
10	4	1193	1201-
10-	4	88	257 *
0	5	976	1014
1	5	169	261-
1-	5	1470	1740
2	5	1299	1606-
2-	5	575	480-
3	5	630	663-
3-	5	1360	1634
4	5	472	426-
4-	5	1509	1602-
5	5	118	245-*
5-	5	1843	1934-
6	5	428	536-
6-	5	651	416
7	5	515	506-
7-	5	442	392
8	5	184	105
8-	5	356	342
9	5	158	29-
9-	5	688	449
10-	5	437	384
0	6	673	696
1	6	381	247
1-	6	937	920
2	6	346	166-
2-	6	904	901-
3	6	1113	1029-
3-	6	657	706-
4	6	454	267
4-	6	743	701
5	6	1209	1301-
5-	6	408	453
6	6	551	705-
6-	6	875	807
7	6	112	97-*
7-	6	369	364
8	6	763	546
8-	6	933	664
9	6	83	29 *
9-	6	1017	835
10-	6	704	725-
0	7	961	964
1	7	1692	2157-
1-	7	111	150 *
2	7	413	387-
2-	7	584	571
3	7	1443	1775
3-	7	199	292
4	7	532	483-
4-	7	670	431-
5	7	1160	1279
5-	7	291	156
6	7	429	458-
6-	7	1249	1280
7	7	107	264-*
7-	7	114	204-*
8	7	187	159-
8-	7	970	870
9	7	72	475-*
9-	7	696	448
10-	7	69	70-*
0	8	1126	1284
1	8	1937	2409
1-	8	492	292-
2	8	673	507-
2-	8	202	205
3	8	1072	1145-
3-	8	118	188-*
4	8	489	408
4-	8	429	404-
5	8	984	1071
5-	8	770	707
6	8	269	446
6-	8	944	907-
7	8	423	428-
7-	8	752	677
8	8	84	126-*
8-	8	650	499-
9-	8	414	328
0	9	444	443
1	9	772	681-
1-	9	687	577
2	9	1245	1690
2-	9	119	3 *
3	9	488	510
3-	9	119	123 *
4	9	116	143 *
4-	9	443	433
5	9	272	52-
5-	9	116	10 *
6	9	325	54-
6-	9	700	498-
7	9	90	820-*
7-	9	691	724-
8	9	69	232 *
8-	9	834	757
9-	9	722	592
0	10	920	1071-
1	10	820	804
1-	10	119	197-*
2	10	837	962-
2-	10	118	174-*
3	10	229	136-
3-	10	407	414
4	10	111	233 *
4-	10	777	748
5	10	803	848
5-	10	801	687-

Table 2 (*cont.*)

k = 3

6	10	1044	1151	
6-	10	106	152	*
7	10	241	203-	
7-	10	947	871	
8-	10	587	431-	
0	11	115	94-	*
1	11	1010	971-	
1-	11	115	68	*
2	11	224	220-	
2-	11	1127	1093-	
3	11	108	59-	*
3-	11	645	693	
4	11	730	561	
4-	11	598	566	
5	11	581	567	
5-	11	1375	1307-	
6	11	249	12-	
6-	11	755	718-	
7-	11	630	575-	
8-	11	188	113	
0	12	730	551	
1	12	1420	1631-	
1-	12	377	281	
2	12	293	177	
2-	12	241	232	
3	12	851	824	
3-	12	732	686-	
4	12	604	398-	
4-	12	681	593-	

k = 3

5	12	78	54	*
5-	12	616	574-	
6-	12	361	192-	
7-	12	69	88	*
0	13	779	693	
1	13	1168	1307-	
1-	13	382	314	
2	13	1321	1553-	
2-	13	756	684-	
3	13	557	453	
3-	13	1131	1202	
4	13	322	344	
4-	13	89	82	*
5-	13	81	16	*
6-	13	346	248-	
1	14	929	942-	
1-	14	615	564	
2	14	949	909-	
2-	14	605	591	
3-	14	191	77-	

k = 4

0	0	2104	1809	
1	0	742	904	
2	0	622	688-	
3	0	266	444-	*
4	0	563	978	
5	0	799	643-	
6	0	207	42	*

k = 4

0	1	1244	1043-	
1	1	594	556	
2	1	653	573-	
2-	1	266	172	*
3	1	266	155	*
3-	1	266	137-	*
4	1	266	29	*
4-	1	266	10	*
5	1	238	268-	*
5-	1	238	113-	*
6	1	1066	944	
6-	1	207	446-	*
7	1	1423	1437	
7-	1	177	374-	*
0	2	949	678	
1	2	594	380	
1-	2	266	282	*
2-	2	266	413-	*
3	2	266	215	*
4	2	681	495	
5	2	1720	1588-	
6	2	207	36-	*
6-	2	207	133-	*
7	2	1334	1536-	
7-	2	177	118-	*
0	3	266	366	*
1	3	266	126-	*
1-	3	266	93-	*

k = 4

2	3	266	446	*
2-	3	266	339	*
3	3	266	165-	*
4	3	238	454-	*
4-	3	1244	1253-	
5	3	238	3-	*
5-	3	238	448	*
6	3	1868	1478-	
6-	3	238	648	*
7	3	889	977	
7-	3	801	690-	
0	4	830	906-	
1	4	266	426-	*
1-	4	266	304	*
2	4	266	143-	*
2-	4	266	488	*
3	4	266	3-	*
3-	4	845	895-	
4	4	594	631-	
4-	4	1216	981-	
5	4	1334	1221-	
5-	4	1718	1911	
6	4	177	115-	*
6-	4	207	356-	*
7	4	207	405	*
0	5	266	46	*
1	5	238	100-	*
1-	5	266	490	*
2	5	238	340	*
2-	5	266	74-	*
3	5	1600	1071-	

k = 4

3-	5	1482	1323-	
4-	5	830	800-	
5	5	238	75-	*
5-	5	238	142	*
6	5	207	4	*
6-	5	799	1009	
0	6	238	306-	*
1	6	2519	2313	
2	6	238	28-	*
2-	6	238	299-	*
3	6	238	324	*
3-	6	1214	1125-	
5	6	177	255-	*
6	6	148	221-	*
0	7	889	771-	
1	7	238	427-	*
1-	7	1423	1252	
2	7	1273	1153	
2-	7	238	390	*
3	7	189	318-	*
3-	7	207	30	*
4	7	207	122-	*
4-	7	978	807	
5	7	148	56	*
5-	7	177	129-	*
0	8	1037	1277	
1-	8	1066	1142-	

available. Two cycles of structure factor calculations followed by three-dimensional Fourier syntheses of electron density gave slightly revised atomic positions. Two cycles of differential syntheses and structure factors in which individual isotropic thermal parameters were introduced reduced R to 0·20. These calculations were done on an IBM 650 computer with Shiono's programs (1957). Since the estimated standard deviations in the atomic y parameters were found to be somewhat larger than in the x and z parameters, the $h4l$ data were collected with the use of counter methods. Unfortunately, the only available crystal was lost before data collection was completed, and it was necessary to scale the counter data to the photographic data by means of the common $h40$ and $h41$ reflexions. The combined data were used in two cycles of a full-matrix least-squares refinement with a Hughes weighting scheme, by means of Busing & Levy's program (1959) for the IBM 704 computer. For each atom an isotropic thermal parameter was varied. The R index was reduced to 0·187. It appeared that the strong intensities of low order (indicated by an asterisk in Table 2) were subject to X-ray extinction, and these were assigned zero weight in the subsequent refinement.

There were also systematic discrepancies between observed and calculated structure factors in the layers $k=0$ through 4 which could be attributed to a combination of the effect of anisotropic thermal vibrations of the atoms and inaccuracy in the interlayer scaling factors arising from the inadequate number of measured common reflexions between layers. The atomic vibrations were expected to have maximum amplitude approximately normal to the planes containing the barbiturate ions, *i.e.* in a direction which makes an angle of about 32° with b. This type of thermal motion should cause systematic diminution in the observed structure amplitudes similar to the effect of applying different scale factors for the layers $k=0$ through 4. In the absence of reliable experimental scaling factors for these layers, the refinement of anisotropic thermal parameters, particularly the B_{22} parameters, was considered to be unjustifiable and in the subsequent refinement the individual scaling factors for the layers $k=0$ through 4 were the only new parameters to be introduced.

Two further cycles of least squares reduced R to 0·160. The values assumed by the scaling factors (as applied to the observed data) increase with k, indicating that these factors are indeed compensating to some extent for the effects of anisotropic thermal motion as described above. Associated with these changes in scaling factors, the changes in atomic positional parameters were in general negligible, being of the order of $0{\cdot}1\sigma$. However, there were a few larger changes, the largest being $1{\cdot}2\sigma$ in $y(\mathrm{N}(1))$, $0{\cdot}5\sigma$ in $y(\mathrm{C}(6))$ and $x(\mathrm{C}(2))$. It was found that all the isotropic thermal parameters had decreased by about 0·4 Å². Although it might be expected that the thermal parameters would have little physical significance, their relative magnitudes are more or less in agreement with what might be expected for a barbiturate ion librating as a rigid body about its center of mass, *i.e.* the thermal parameters for the outer oxygen atoms are 1·7, 1·9 and 2·2 Å² while for the atoms of the ring they range between 1·1 and 1·5 Å².

A final difference Fourier synthesis in three dimensions was calculated on the IBM 1620 computer by means of Hall's program (unpublished) in order to seek the hydrogen atoms. Reflexions for which $\sin\theta/\lambda \geq 0{\cdot}5$, together with those considered to be affected by X-ray extinction, were omitted from the calculations. The highest peaks in this difference Fourier synthesis (Fig. 1(*b*)) were approximately in the positions expected to be occupied by hydrogen atoms, except for H(5). The displacement of this peak by 0·3 Å from the best least-squares plane of the pyrimidone ring (Table 4) has no apparent justification on the grounds of stereochemistry or molecular packing. The residual electron density near other

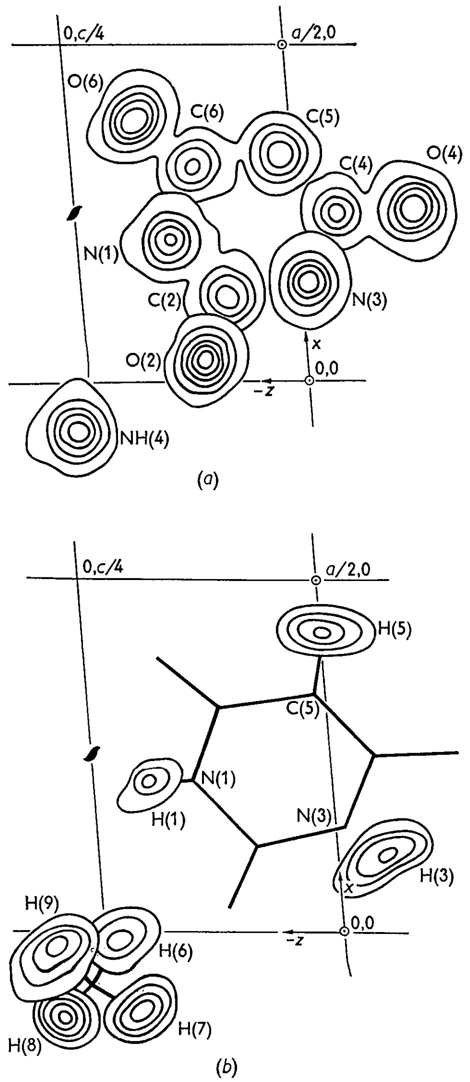

Fig. 1. (*a*) The final electron density map composed from sections of the three-dimensional Fourier synthesis. Contours are at intervals of 2 e.Å^{-3} with the zero contour omitted. (*b*) The residual electron density map showing the peaks attributed to the hydrogen atoms. This map was composed from sections of the final three-dimensional difference Fourier synthesis. Contours are at intervals of 0·05 e.Å^{-3} with the lowest contour at 0·20 e.Å^{-3}.

atoms indicated that thermal motion normal to the plane of the barbiturate ion had only approximately been taken into account. The hydrogen atoms were included in the final structure factor calculations with positional parameters derived from the difference Fourier synthesis and isotropic thermal parameters which were assumed to be comparable to those of the atoms to which they are bonded. The final *R* index was 0·150.

The results of these calculations are shown in Table 2, in which asterisks indicate those reflexions which were unobserved or omitted from the least-squares refinement. The layer scaling factors and atomic positional and thermal parameters are listed in Table 3 with their estimated standard deviations as derived from the least-squares refinement. The r.m.s. estimated standard deviation in atomic parameters are $\sigma(x)=0{\cdot}0043$, $\sigma(y)=0{\cdot}0045$, $\sigma(z)=0{\cdot}0045$ Å and $\sigma(B)=0{\cdot}092$ Å^2. The estimated standard deviation in a bond length is 0·011 Å and in a bond angle is 0·8°. The best least-squares plane through the atoms of the barbiturate ion (excluding the hydrogen atoms) is given in Table 4 together with the distances of various atoms from this plane. The molecular para-

Table 3. *The structure parameters with their e.s.d.'s*

(*a*) The scale factors derived from the least-squares refinement. These have been applied to the listed values of $|F(\text{obs.})|$ in Table 2

Layer	S_R	$\sigma(S_R)$
h0l	0·979	0·021
h1l	1·119	0·015
h2l	1·148	0·016
h3l	1·260	0·018
h4l	1·686	0·022

(*b*) The atomic parameters. The e.s.d.'s in positional parameters have been multiplied by 10^4 and $\sigma(B)$ has been multiplied by 10^2

Atom	*x/a*	σ(*x*)	*y/b*	σ(*y*)	*z/c*		*B* (Å^2)	σ
C(2)	0·1215	4	0·809	13	−0·0861	3	1·13	9
C(4)	0·2477	4	0·533	13	0·0447	3	1·35	10
C(5)	0·3353	5	0·423	13	−0·0176	3	1·47	10
C(6)	0·3151	4	0·503	12	−0·1138	3	1·29	9
N(1)	0·2081	4	0·695	11	−0·1425	3	1·24	9
N(3)	0·1437	4	0·720	11	0·0063	3	1·30	9
N$^+$	−0·0714	4	0·440	12	−0·2682	3	1·80	10
O(2)	0·0302	3	0·982	10	−0·1173	3	1·73	9
O(4)	0·2556	4	0·475	11	0·1310	3	2·21	10
O(6)	0·3833	3	0·414	10	−0·1740	3	1·87	9
H(1)	0·203		0·75		−0·196		1·24	
H(3)	0·105		0·82		0·048		0·30	
H(5)	0·423		0·35		0·010		1·47	
H(7)	−0·015		0·29		−0·233		1·80	
H(8)	−0·112		0·53		−0·223		1·80	
H(9)	−0·120		0·33		−0·305		1·80	
H(10)	−0·030		0·40		−0·300		1·80	

Table 4

(*a*) Equation of best least-squares plane through the atoms* of the barbiturate ion

$$-0{\cdot}5081+0{\cdot}8460y-0{\cdot}1166z=0{\cdot}1015$$

Note: The coordinates *x*, *y*, and *z* are expressed in Å and are referred to the crystallographic axes

(*b*) Distance of various atoms from this plane

Atoms included in calculation of plane*		Atoms not forming the plane	
Atom	*d*	Atom	*d*
N(1)	−0·001 Å	H(1)	−0·06 Å
C(2)	0·002	H(3)	−0·17
O(2)	−0·011	H(5)	−0·30
N(3)	0·020		
C(4)	−0·001	O(2′)(· · · N(3))	−0·19
O(4)	0·000	O(6′)(· · · N(1))	0·09
C(5)	−0·016		
C(6)	−0·006		
O(6)	0·012		

* *The atoms are those whose coordinates are listed in* Table 3.

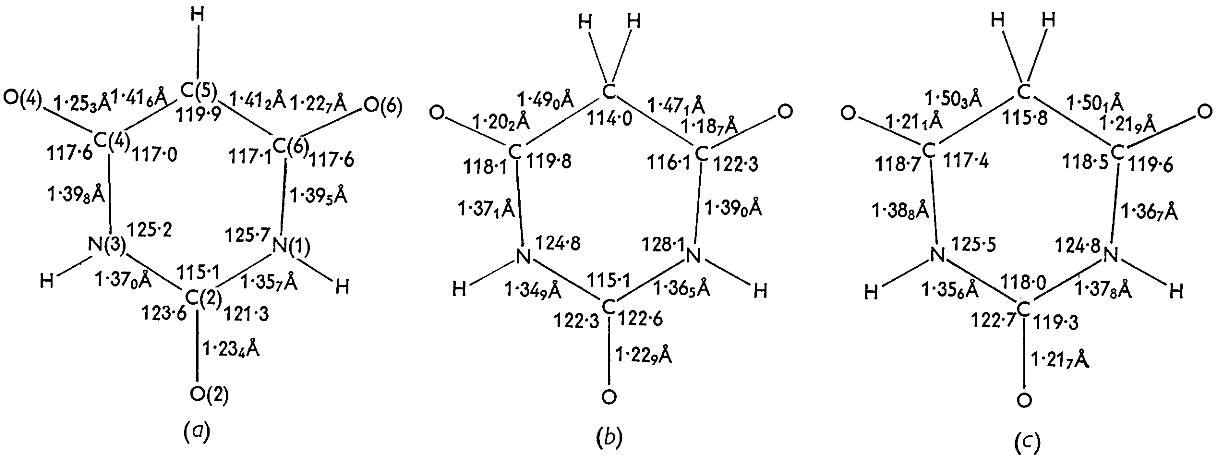

Fig. 2. The observed bond lengths and angles. (*a*) The barbiturate ion. (*b*) The barbituric acid molecule as determined from the crystal structure of the dihydrate (Jeffrey *et al.*, 1961). (*c*) The barbituric acid molecule as determined from the structure of the anhydrous crystals (Bolton, 1963).

meters were calculated by means of programs by Chu (unpublished) for the IBM 1620 computer.

Discussion of the structure

The barbiturate ion

In Fig. 2 are shown the bond lengths and angles for barbituric acid as determined from the anhydrous crystals (Bolton, 1963) and the dihydrate (Jeffrey *et al.*, 1961) together with those presently determined for the barbiturate ion.

The preferred ring position for substitution of hydrogen in barbiturates is at C(5) (Levina & Velichko, 1960) and it would be expected that the barbiturate ion would form by loss of a proton from C(5). This has been observed in the crystal structure of ammonium barbiturate. The largest observed distortions of the barbiturate ion from a coplanar structure with

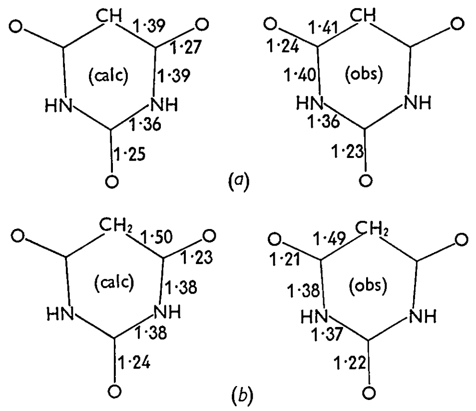

Fig. 3. The observed and predicted bond lengths. (*a*) The barbiturate ion. (*b*) The barbituric acid molecule.

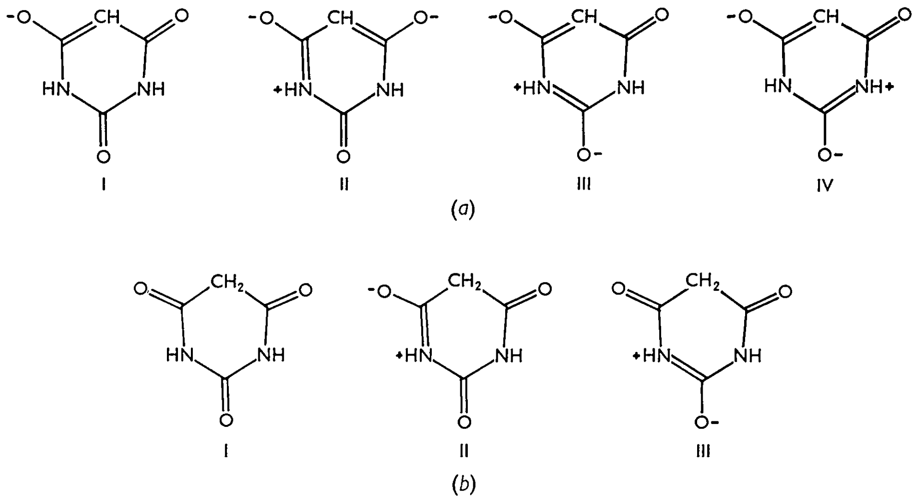

Fig. 4. The valence bond structures. Only non-symmetry-related structures are shown. All contributing structures were assigned unit weight except those denoted by (I), which were assigned double weight. (*a*) The barbiturate ion. (*b*) The barbituric acid molecule.

point symmetry $2mm$ are the discrepancies between the bond lengths C(4)–O(4) (1·25 Å) and C(6)–O(6) (1·23 Å), between the bond angles N(3)C(2)O(2) (123·5°) and N(1)C(2)O(2) (121·3°) and the displacement from coplanarity of atoms H(5) (0·3 Å), C(5) (0·16 Å) and N(3) (0·020 Å). All these distortions are of doubtful significance.

The observed bond lengths in barbituric acid and the barbiturate ion are compared in Fig. 3 with those predicted on the basis of a superposition of valence bond structures according to Pauling's theory (1960). The observed bond lengths shown in Fig. 3 are averages of the lengths of symmetry-related bonds, assuming a central mirror plane through O(2), C(2) and C(5) in the molecules of both the acid and the ion. The calculated bond lengths were derived from a superposition of the valence bond structures of Fig. 4, together with mirror-symmetry-related structures. All these structures were given equal weight except those shown as (I) and these were given double weight. The bond lengths assumed for bond orders 1·0 and 2·0 are listed in Table 5. For bonds of intermediate order, lengths were calculated using Pauling's expression (1960). The results show agreement between predicted and observed lengths which is as good as can be expected.

Table 5. *Data used in the calculation of bond lengths*

Bond type	Length	Source
$C(sp^2)-C(sp^2)$	1·48 Å	Most probably values estimated by Lide (1961) from recent spectroscopic and electron diffraction data
$C=C$	1·33	
$C(sp^2)-C(sp^3)$	1·50	
$C-O^-$	1·34	Estimated from Pauling's (1960) covalent radii with allowances for formal charge and state of hybridization
$C=O$	1·22	
$C(sp^2)-N(sp^2)$	1·41	
$C=N^+$	1·24	

The greatest observed differences in structure between the barbituric acid molecule and its ion were in the bonds formed by C(5). Thus in barbituric acid these bonds are typical of a predominantly tetrahedral hybridization for C(5), since the bond lengths to adjacent carbon atoms (1·49 Å) are close to the predicted value of 1·50 Å for a $C(sp^3)$–$C(sp^2)$ bond length and the angle between these bonds is 115°. In the barbiturate ion, the shortening of these bonds is attributed to the change to a predominantly trigonally hybridized C(5) and also to the effect of electron delocalization which requires these bonds to be of order 1·5. The bond angle C(4)C(5)C(6) in the barbiturate ion was found to have increased to the trigonal angle (120°).

The experimental accuracy makes any further discrepancies between the structures of barbituric acid and its ion of only doubtful significance. It is pointed out that the corresponding C–O bond lengths appear somewhat longer in the ion than in the acid, which is to be expected from the increased $C-O^-$ character in the bonds. In the barbiturate ion, the N(1)–C(6) and N(3)–C(4) bonds appear longer (1·40 Å) than the N(1)–C(2) and N(3)–C(2) bonds (1·36 and 1·37 Å). In the parent acid, there seems to be no systematic variation in the N–C bond lengths and the averages of the lengths (N(1)–C(6), N(3)–C(4)) and (N(1)–C(2), N(3)–C(2)) are almost equal.

The molecular packing and hydrogen bonding

The crystal structure of ammonium barbiturate consists of a compact three-dimensional network of NH $\cdots$ O hydrogen bonded ammonium and barbiturate ions (Fig. 5). Barbiturate ions are hydrogen bonded in almost coplanar dimers. These dimers are stacked along *b* with the molecular planes in adjacent stacks oppositely inclined. There is a spiral configuration of hydrogen bonds linking adjacent stacks and these stacks are further hydrogen bonded through the ammonium ions. The close intermolecular distances are listed in Table 6.

Those barbiturate ions which are hydrogen bonded in pairs across a crystallographic center of symmetry are not exactly coplanar, since the best least-squares planes through atoms of each of the barbiturate ions (excluding the hydrogen atoms) are separated by 0·20 Å. The hydrogen bonds N(3) $\cdots$ O(2) are of length 2·80 Å, the H(3) $\cdots$ O(2) distance is 1·98 Å and the angle N(3)H(3) $\cdots$ O(2) is 163°.

The hydrogen bonds N $\cdots$ O which link barbiturate ions in a spiral configuration about the twofold screw axes are somewhat weaker. They are of length 2·86 Å, the H(1) $\cdots$ O(6) distance is 2·10 Å and the angle N(1)H(1)O(6) is 158°. The atom O(6) of the acceptor barbiturate ion lies 0·09 Å out of the plane of the donor barbiturate ion.

The ammonium ions are in stacks running parallel

Table 6. *Intermolecular distances*

(*a*) Hydrogen bonding distances

N(3)H(3) $\cdots$ O(2) (II)	2·80 Å
N(1)H(1) $\cdots$ O(6) (III)	2·86
N^+H(8) $\cdots$ O(4) (IV)	2·76
N^+H(9) $\cdots$ O(6) (III)	2·89
N^+H(7) $\cdots$ O(4) (V)	2·92
N^+H(6) $\cdots$ O(2) (VI)	2·93

(*b*) Non bonding distances

N^+H(9) $\cdots$ O(6) (VIII)	3·02 Å
N^+H(6) $\cdots$ O(2) (I)	3·13
N^+H(8) $\cdots$ O(4) (VII)	3·18
C(5) $\cdots$ C(5) (X)	3·56
C(5) $\cdots$ N(1) (VI)	3·33
C(4) $\cdots$ N(3) (VI)	3·35
C(2) $\cdots$ O(2) (VI)	3·35
C(2) $\cdots$ C(5) (IX)	3·38
N(1) $\cdots$ O(2) (VI)	3·38

Note: The left hand member of each pair of atoms has parameters (x, y, z) corresponding to those listed in Table 3. The parameters for the atom on the right are indicated as follows:

(I) x, y, z
(II) $x, 2-y, z$
(III) $\frac{1}{2}-x, \frac{1}{2}+y, -\frac{1}{2}-z$
(IV) $-\frac{1}{2}+x, \frac{1}{2}-y, -\frac{1}{2}+z$
(V) $-x, 1-y, -z$
(VI) $x, -1+y, z$
(VII) $-\frac{1}{2}+x, \frac{3}{2}-y, -\frac{1}{2}+z$
(VIII) $\frac{1}{2}-x, \frac{3}{2}+y, -\frac{1}{2}-z$
(IX) $x, 1+y, z$
(X) $1-x, 1-y, -z$

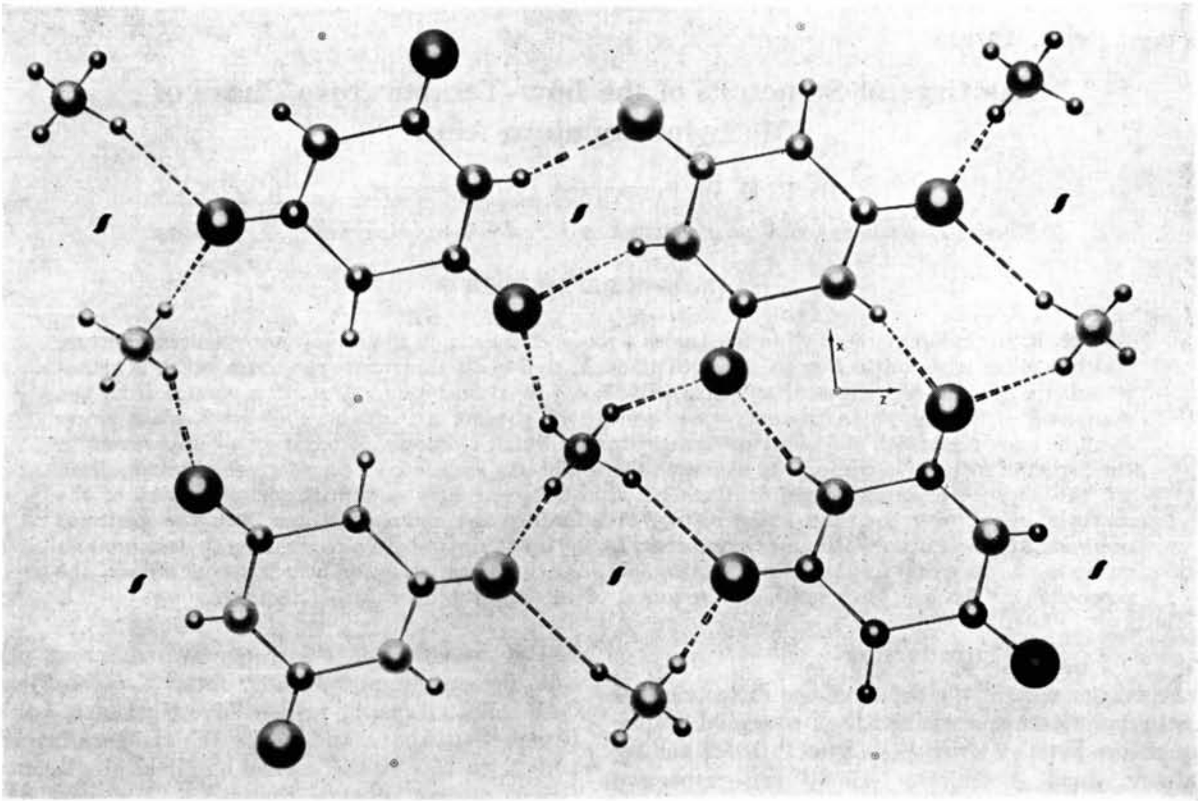

Fig. 5. The crystal structure of ammonium barbiturate viewed along *b*.

to *b*, separated by the lattice translation of 3·85 Å. Each ammonium ion may be said to be at the center of a distorted cube with oxygen atoms at six of the corners of the cube and a seventh oxygen atom at the midpoint of the side joining the remaining two corners. All seven of these oxygen atoms belong to different barbiturate ions. The N · · · O distances range between 2·76 and 3·18 Å and the O · · · N · · · O′ angles range between 78° and 132°. The geometry of this arrangement is such that it is impossible to form four hydrogen bonds which subtend approximately tetrahedral angles at the ammonium nitrogen atom. Within probable experimental error, the ammonium ion is of regular tetrahedral form since the N–H bond lengths were observed to be 0·83, 0·88, 0·91 and 0·95 Å and the H–N–H angles were found to range between 100° and 115°. The ammonium ion forms three very bent hydrogen bonds of length 2·89, 2·92 and 2·93 Å with N–H · · · O angles of 151°, 153° and 156° and H · · · O distances of 2·06, 2·11 and 2·04 Å respectively, while the fourth and shortest hydrogen bond (2·76 Å) is less bent with an angle N–H(8) · · · O(4) of 168°. The distance H(8) · · · O(4) is 1·99 Å. Thus the observed orientation of the ammonium ion results in every oxygen atom accepting two hydrogen bonds.

There are no unusually close intermolecular approaches in this crystal structure, other than those already discussed. The best least-squares planes through neighbouring barbiturate ions related by the lattice translation *b* are separated by 3·25 Å, which is slightly larger than the intersheet distance in barbituric acid dihydrate (3·12 Å). The closest distance C(5) · · · C(5′) between neighbouring ions related by a crystallographic center of symmetry is 3·56 Å.

This work was supported by a research grant (B-2763) from the U.S. Public Health Service, National Institutes of Health.

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