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The Crystal Structure of Anhydrous Barbituric Acid

BY WILLIAM BOLTON
The Crystallography Laboratory, The University of Pittsburgh, Pittsburgh 13, *Pa., U.S.A.*

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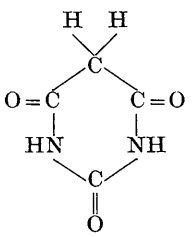
The crystal structure of anhydrous barbituric acid has been determined by a three dimensional Fourier transform method and refined by least squares with anisotropic temperature parameters. The molecules are joined in a hydrogen bonded system which involves all electronegative atoms except a carbonyl oxygen. This atom is involved in a close intermolecular approach, with a ring carbon atom, of 2·90 Å, in a similar orientation to the close approaches in parabanic acid (Davies & Blum, 1955) and chloranil (Chu, Jeffrey & Sakurai, 1962).

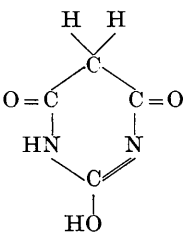
Bond lengths and angles are the same as those in barbituric acid dihydrate (Jeffrey, Ghose & Warwicker, 1961) within the limits of the analyses. The molecule in anhydrous barbituric acid is significantly distorted from planarity however, and this can be attributed to crystal field forces.

Introduction

Although the literature on barbituric acid and its derivatives is very extensive, there are no data relating specifically to an anhydrous form. The dihydrate, which is obtained by crystallization from aqueous solution, was reported by Baeyer in 1863, and its crystal structure was determined by Jeffrey, Ghose & Warwicker (1961). In the dihydrate, the molecules are in the tri-keto form, I, and the six protons in the asymmetric unit are involved in an intermolecular hydrogen-bond arrangement which includes all the amino groups and the oxygen atoms. In the anhydrous crystal there are three carboxyl oxygens and two amino nitrogens with protons available for only two hydrogen bonds. Therefore an intermolecular bonding system which includes all the carbonyl and amino groups is not possible and, in this sense, the anhydrous structure is proton deficient for hydrogen-bonding relative to the hydrate. Three possibilities can be envisaged. One, that the molecules adopt the mono- or di-enolic form, II or III, thereby increasing the number of protons available for hydrogen-bonding; second, that a single proton is associated with more than one carbonyl and one amino interaction, *i.e.* in a bifurcated bond; and third, that only two hydrogen bonds are in fact formed.



I



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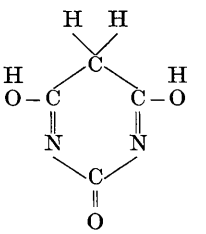

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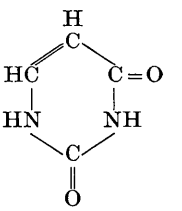
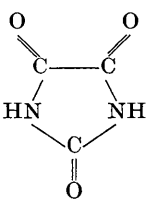


IV



V

In uracil, IV, where there is a similar situation, Parry (1954) found that one carbonyl oxygen forms two hydrogen bonds and the other none, with normal van der Waals separations of about 3·2 Å. In parabanic acid, V, on the other hand, where there are also more intermolecular contacts between carbonyl and amino groups than protons available, Davies & Blum (1955) observed some short intermolecular separations, comparable in length with hydrogen-bond distances.

The purpose of this investigation was to determine the tautomeric form of the barbituric acid molecules in the anhydrous crystals and the nature of their intermolecular association.

Experimental

Barbituric acid crystallizes easily from aqueous solutions as the dihydrate and the anhydrous compound is obtained as a powder by drying this at 100 °C. It is only slightly soluble in alcohol and acetone and is insoluble in many non-polar liquids. Small single crystals were obtained from a solution of dry ethanol saturated at the boiling point by standing at 0 °C. for several days. These were short monoclinic prisms slightly elongated about the c axis with the forms {100}, {010} and {001}. In contrast to the dihydrate, the crystals are stable in air. No cleavage was observed.

The unit-cell dimensions, measured with a G.E. single crystal orienter, are

$$a = 6{\cdot}817 \pm 0{\cdot}005,\ b = 14{\cdot}310 \pm 0{\cdot}005,$$
$$c = 6{\cdot}248 \pm 0{\cdot}005 \text{ Å};\ \beta = 118° 34' \pm 6'.$$

From the systematic extinctions, $0k0$ absent with k odd, $h0l$ absent with l odd, the space group is $P2_1/c$. With $Z=4$, $D_x = 1{\cdot}574$ g.cm.$^{-3}$, and $D_m = 1{\cdot}560$ g.cm.$^{-3}$.

The intensities were recorded on multiple-film Weissenberg photographs with Cu $K\alpha$ radiation. Zero to three layers about a, zero to four about b and zero to five about c were observed. The intensities were correlated by means of the double-slit technique (Stadler, 1950), and reduced to the observed amplitudes by the graphical method (Cochran, 1948). A total of 770 reflexions out of the possible 1210 were observed. No corrections were applied for absorption. The intensities were put on an absolute scale by Wilson's statistical method (Wilson, 1942) and the scale factor so obtained agreed with the final scale factor within two per cent.

The structure determination

The structure was solved by the three-dimensional molecular transform method. The Fourier transform of a projected molecule was calculated by assuming a regular hexagonal arrangement of stationary point atoms of equal scattering power. The molecular structure factor expression is:

$$A + iB = \cos 4J + 4 \cos J \cos E + 2 \cos 2J\ (\cos 2E + 1) + i(2 \sin 2J \cos 2E - \sin 4J),$$

where J and E are reciprocal space vectors of magnitude 2·2 and 1·2 reciprocal space units, corresponding to the real space vectors j and e (Fig. 1) of length $\frac{1}{2}.1{\cdot}4$ Å and $\sqrt{\frac{3}{2}}.1{\cdot}4$ Å, respectively. The components A and B were calculated separately with Beevers–Lipson strips, for J in thirtieths and E in fifteenths.

The modulus $\sqrt{(A^2+B^2)}$, which was used in subsequent transform fitting procedures is shown on Fig. 1. It bears a strong resemblance to the benzene Fourier transform having a peak at the origin and a hexagonal array of surrounding peaks. The main

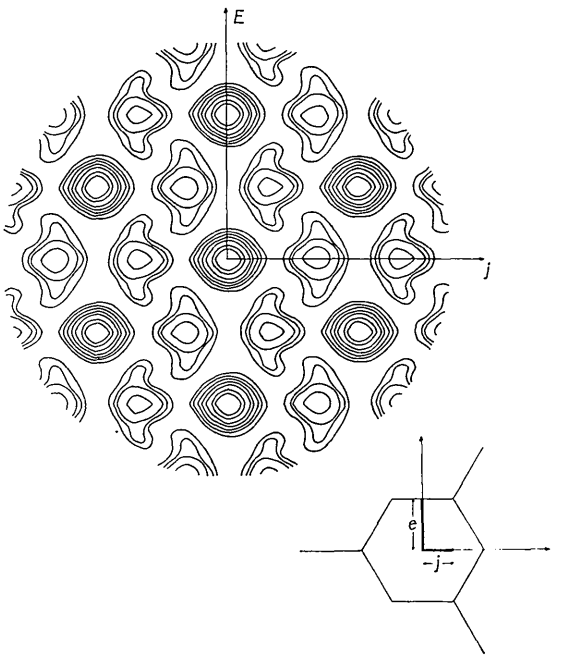


Fig. 1. The modulus $\sqrt{(A^2+B^2)}$ of the Fourier transform of an idealized barbituric acid molecule.

features of the three-dimensional transform of a single molecule are correspondingly a set of six cylinders arranged hexagonally round a similar cylinder passing through the origin (Kenyon & Taylor, 1953).

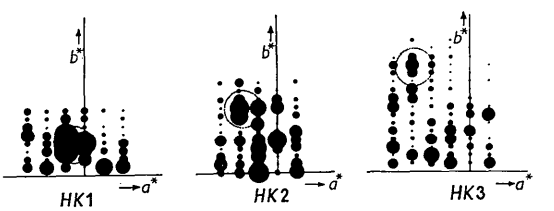


Fig. 2. Part of the weighted reciprocal lattice of barbituric acid. Dotted circles show the positions of the transform origin peaks.

The examination of sections of the three-dimensional weighted reciprocal lattice, shown in Fig. 2, led to the identification of the transform origin peak on the $HK1$, $HK2$ and $HK3$ sections (Stadler, 1960), despite the coarseness of the reciprocal lattice net. This gave the orientation of the axis of the transform of a single molecule in reciprocal space and consequently the orientation of the molecular plane in real space. This was such that in the most clearly resolved projection, on (001), a molecule was foreshortened by tilting out of the plane by 62°. The plane transform of such a projected molecule is a section through the cylindrical three-dimensional transform and was easily derived by extending the plane transform shown in Fig. 1 about a direction parallel to the direction of

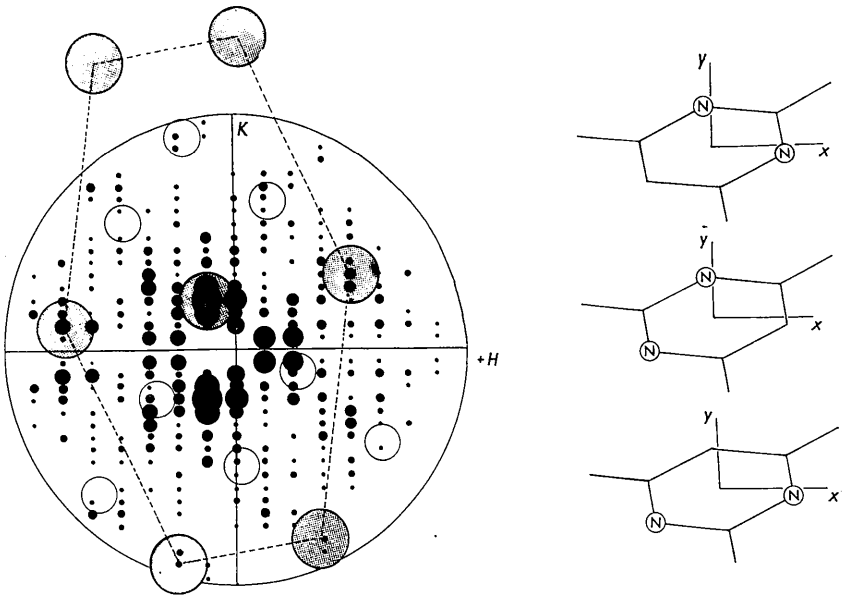


Fig. 3. Transform fit on the $HK1$ weighted reciprocal lattice section of barbituric acid. Only the strongest peaks of the transform are shown. The resulting orientations for a projected molecule are shown alongside.

maximum foreshortening of a projected molecule by a factor 1/cos 62°.

Fitting this plane transform to the $HK1$, $HK2$ and $HK3$ weighted reciprocal lattice sections gave three possible orientations for a molecule in the (001) projection, because of the six-fold symmetry of the transform due to the assumption of identical atoms. The transform fit on $HK1$ with the resulting molecular orientations is shown in Fig. 3.

The (X, Y) coordinates of the molecular centre were found by the method of Taylor & Morley (1959). The quantity $\Sigma||F_o|-|F_G||$ was evaluated throughout the unit cell for several reflexions, where F_G is the value of a structure factor calculated in terms of the central coordinates of one molecule and the value of the Fourier transform for that reflexion (see the appendix). Fig. 4 represents the results of this calculation for six $h00$ and six $0k0$ reflexions and from this it can be seen that best agreement between $|F_o|$ and $|F_G|$ occurs when the molecule is centred at $X_c=0{\cdot}340$, $Y_c=0{\cdot}115$. With a single molecule of the asymmetric unit on this position it was possible to identify one of the ring atoms as nitrogen by assuming carbonyl–imino hydrogen bonding across a centre of symmetry.

Structure factors calculated for this trial arrangement gave an agreement index of 48% and small movements of the whole molecule reduced this to 33% for all the $hk0$ reflexions.

The remaining parameter, the Z coordinate of the centre of the molecule, was found by packing the molecules into a hydrogen-bonded arrangement, giving a trial structure with an agreement index of 34% for all $0kl$ reflexions.

As none of the projections were well-resolved the refinement of the structure was carried out on the three-dimensional data. The first structure factor calculation, which included unobserved reflexions, gave an R value of 33% and in two cycles of refinement by differential synthesis, using an IBM 650 program of Shiono (1959), this was reduced to 18%.

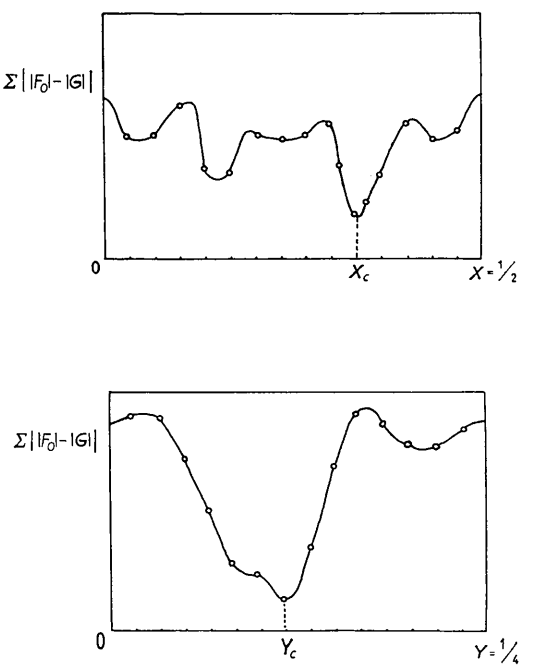


Fig. 4. $\Sigma||F_o|-|F_G||$ evaluated for six $h00$ and six $0k0$ reflections. The minima occur at X_c and Y_c, the coordinates of the centre of a molecule in the (001) projection.

Table 1

H	K	FOBS	ACAL
L = 0			
0	2	233	269
0	4	619	-738
0	6	130	-141
0	8	22	-21
0	10	25	25
0	12	80	-76
0	14	8	0
0	16	7	1
1	0	403	-434
1	1	422	476
1	2	64	-66
1	3	9	14
1	4	161	-178
1	5	197	-240
1	6	33	22
1	7	31	-36
1	8	191	236
1	9	124	-136
1	10	7	11
1	11	76	-78
1	12	8	-13
1	13	8	-9
1	14	44	-39
1	15	47	46
1	16	7	-13
2	0	235	236
2	1	93	-100
2	2	113	-117
2	3	225	254
2	4	292	-325
2	5	16	-3
2	6	115	-133
2	7	90	-90
2	8	130	135
2	9	176	187
2	10	137	123
2	11	64	59
2	12	8	-24
2	13	8	-5
2	14	8	3
2	15	39	-39
2	16	39	40
3	0	267	246
3	1	119	125
3	2	81	80
3	3	152	-155
3	4	142	149
3	5	24	-27
3	6	44	49
3	7	150	156
3	8	135	-138
3	9	15	13
3	10	46	-39
3	11	8	11
3	12	8	4
3	13	8	-1
3	14	8	-16
3	15	8	16
3	16	39	-35
4	0	122	-128
4	1	9	-7
4	2	131	133
4	3	46	38
4	4	7	7
4	5	7	-9
4	6	144	-140
4	7	59	-56
4	8	31	30
4	9	85	-85
4	10	31	25
4	11	85	-86
4	12	9	-8
4	13	8	-6
5	0	159	-149
5	1	219	-227
5	2	151	-159
5	3	174	-195
5	4	46	40
5	5	103	114
5	6	76	71
5	7	86	92
5	8	9	9
5	9	9	10
5	10	46	48
5	11	8	7
6	0	157	159
6	1	9	3
6	2	82	79
6	3	41	-35
6	4	57	-58
6	5	62	55
6	6	38	-33
6	7	84	79
6	8	19	-16
6	9	19	-16
6	10	40	-29
7	0	14	22
7	1	101	-91
7	2	9	12
7	3	88	-73
7	4	16	-15
7	5	25	23
7	6	6	-1
7	7	27	20
7	8	19	32
L = 1			
0	1	42	-16
0	2	324	330
0	3	269	261
0	4	503	545
0	5	285	-254
0	6	59	66
0	7	159	-142
0	8	167	147
0	9	78	81
0	10	56	-42
0	11	59	57
0	12	90	-85
0	13	8	-8
0	14	36	35
0	15	7	14
1	1	432	424
1	2	19	14
1	3	171	-173
1	4	89	-98
1	5	59	59
1	6	41	43
1	7	6	1
1	8	80	-64
1	9	115	101
1	10	76	56
1	11	39	-35
1	12	44	42
1	13	151	-139
1	14	51	-42
1	15	36	-36
2	1	372	-368
2	2	176	-181
2	3	192	186
2	4	249	-259
2	5	22	-18
2	6	32	-16
2	7	61	52
2	8	29	-23
2	9	37	-30
2	10	85	-89
2	11	34	33
2	12	8	-10
2	13	40	45
2	14	49	39
2	15	7	-26
3	1	63	57
3	2	180	-200
3	3	7	-14
3	4	174	163
3	5	80	-79
3	6	85	89
3	7	150	-154
3	8	44	36
3	9	39	37
3	10	50	45
3	11	39	38
3	12	32	29
3	13	7	20
3	14	6	-21
3	15	70	74
4	1	41	-36
4	2	115	-120
4	3	19	17
4	4	31	22
4	5	167	165
4	6	231	245
4	7	93	96
4	8	8	-22
4	9	98	-92
4	10	98	-97
4	11	49	-49
4	12	21	-28
4	13	5	1
4	14	5	5
5	1	37	29
5	2	134	-150
5	3	8	-13
5	4	134	-133
5	5	59	-59
5	6	55	-55
5	7	29	28
5	8	54	57
5	9	7	-1
5	10	6	-6
6	1	24	-19
6	2	80	-77
6	3	45	-45
6	4	16	12
6	5	7	6
6	6	88	92
6	7	6	-12
6	8	5	29
7	1	46	42
7	2	52	57
7	3	5	6
-1	2	159	-161
-1	3	540	-583
-1	4	698	-855
-1	5	550	-534
-1	6	6	-3
-1	7	221	204
-1	8	108	104
-1	9	194	186
-1	10	7	19
-1	11	8	15
-1	12	8	-5
-1	13	8	-7
-1	14	8	15
-1	15	7	-3
-1	17	44	45
-2	1	334	304
-2	2	78	-86
-2	3	255	-255
-2	4	200	214
-2	5	212	214
-2	6	37	-38
-2	7	86	79
-2	8	95	-86
-2	9	7	-0
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-2	15	34	-32
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-3	1	247	247
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-3	6	258	255
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-3	15	7	14
-4	1	6	-6
-4	2	51	48
-4	3	193	-192
-4	4	92	-85
-4	5	34	23
-4	6	8	6
-4	7	40	-40
-4	8	84	-78
-4	9	39	-36
-4	10	8	-5
-4	11	46	46
-4	12	42	37
-4	13	88	88
-4	14	22	-22
-4	15	32	27
-5	1	8	-14
-5	2	221	-197
-5	3	26	29
-5	4	34	31
-5	5	54	35
-5	6	66	-66
-5	7	47	47
-5	8	61	-65
-5	9	47	45
-5	10	8	8
-5	11	7	-23
-5	12	36	33
-5	13	73	-71
-6	1	38	37
-6	2	234	244
-6	3	111	107
-6	4	94	90
-6	5	54	-57
-6	6	8	-4
-6	7	79	-79
-6	8	34	-29
-6	9	6	4
-7	1	7	-1
-7	2	7	4
-7	3	83	-75
-7	4	47	-44
-7	5	6	-14
-7	6	42	-41
-7	7	6	-3
-7	8	32	32
-8	1	26	22
-8	2	59	58
L = 2			
0	0	93	-70
0	1	28	25
0	2	30	-25
0	3	172	-164
0	4	353	-337
0	5	72	46
0	6	27	-27
0	7	6	11
0	8	240	209
0	9	162	-141
0	10	29	36
0	11	8	-3
0	12	26	29
0	13	8	-4
0	14	49	-45
0	15	7	-1
1	0	358	-339
1	1	218	-200
1	2	60	-62
1	3	176	148
1	4	184	175
1	5	231	220
1	6	7	10
1	7	109	105
1	8	61	-64
1	9	58	59
1	10	9	12
1	11	57	-54
1	12	9	15
1	13	50	44
1	14	7	25
1	15	6	-10
2	0	266	236
2	1	161	-145
2	2	36	47
2	3	344	-303
2	4	43	38
2	5	6	-2
2	6	64	63
2	7	7	7
2	8	8	-24
2	9	8	-17
2	10	62	-53
2	11	136	132
2	12	63	-60
2	13	7	-8
2	14	6	-5
2	15	46	-47
3	0	127	-113
3	1	59	-57
3	2	8	9
3	3	37	-31
3	4	8	7
3	5	38	30
3	6	39	39
3	7	49	45
3	8	71	-75
3	9	81	-80
3	10	120	-109
3	11	144	-154
3	12	123	125
3	13	6	-5
3	14	77	79
4	0	88	-110
4	1	33	-28
4	2	106	-110
4	3	29	-29
4	4	29	36
4	5	9	-2
4	6	55	55
4	7	92	89
4	8	43	37
4	9	96	88
4	10	35	34
4	11	6	-13
4	12	52	-48
5	0	9	6
5	1	46	-40
5	2	51	57
5	3	91	-90
5	4	46	57
5	5	4	32
5	6	7	0
5	7	63	76
5	8	49	-54
6	0	6	-4
6	1	6	3
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-1	5	49	-38
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-1	8	250	-238
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-1	10	119	106
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-1	13	8	-12
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-1	15	6	-13
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-3	0	118	130
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-3	7	93	82
-3	8	37	-38
-3	9	96	-79
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-3	11	53	-46
-3	12	116	110
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-3	14	70	72
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-4	0	251	242
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-4	3	232	-200
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-4	5	39	-42
-4	6	7	4
-4	7	6	5
-4	8	38	42
-4	9	9	2
-4	10	9	11
-4	11	96	-87
-4	12	83	-79
-4	13	6	5
-4	14	5	-14
-4	15	43	33
-5	0	35	31
-5	1	86	85
-5	2	83	76
-5	3	26	18
-5	4	26	-29
-5	5	9	-12
-5	6	27	29
-5	7	49	50
-5	8	9	12
-5	9	65	58
-5	10	108	-94
-5	11	48	45
-5	12	23	23
-6	0	27	19
-6	1	27	-27
-6	2	143	-130
-6	3	32	30
-6	4	66	-69
-6	5	143	128
-6	6	77	66
-6	7	9	5
-6	8	42	41
-6	9	95	-86
-7	0	47	47
-7	1	26	-26
-7	2	89	80
-7	3	7	5
-7	4	7	-14
-7	5	59	-47
-7	6	94	-93
-7	7	114	-102
-7	8	28	-21
-8	0	6	1
-8	1	34	25
L = 3			
0	1	53	61
0	2	51	-47
0	3	110	115
0	4	52	-43
0	5	192	197
0	6	5	16
0	7	149	-138
0	8	114	-109
0	9	55	-63
0	10	36	-30
0	11	21	-19
0	12	30	29
0	13	6	12
0	14	26	-23
0	15	27	30
1	1	221	-229
1	2	74	-63
1	3	127	-121
1	4	46	-46
1	5	5	7
1	6	20	-26
1	7	235	237
1	8	46	-43
1	9	6	-6
1	10	6	10
1	11	30	-30
1	12	5	-0
1	13	33	33
1	14	5	-15
1	15	22	-28
2	1	27	-24
2	2	20	-18
2	3	76	74
2	4	20	-21
2	5	104	112
2	6	30	20
2	7	161	-162
2	8	180	188
2	9	145	-144
2	10	5	11
2	11	34	32
2	12	44	-40
2	13	103	102
2	14	38	37
3	1	47	-52
3	2	39	45
3	3	112	108
3	4	6	-6
3	5	77	87
3	6	53	50
3	7	5	1
3	8	42	-37
3	9	5	3
3	10	31	-35
3	11	34	-38
3	12	30	-33
3	13	43	-57
3	14	9	0
4	1	111	-113
4	2	132	-125
4	3	41	38
4	4	48	-50
4	5	49	49
4	6	5	2
4	7	5	-13
4	8	29	31
4	9	53	-48
4	10	40	-33
4	11	28	0
5	1	34	-33
5	2	5	12
-1	1	235	268
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-1	3	98	-81
-1	4	216	235
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-1	6	96	100
-1	7	61	60
-1	8	122	124
-1	9	7	11
-1	10	48	-47
-1	11	21	-23
-1	12	14	-19
-1	13	32	-34
-1	14	47	51
-1	15	12	-16
-1	16	33	-32
-2	1	222	-224
-2	2	292	-312
-2	3	38	-35
-2	4	190	-197
-2	5	61	-62
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-2	7	5	-3
-2	8	59	-61
-2	9	22	24
-2	10	98	91
-2	11	65	65
-2	12	80	77
-2	13	59	59
-2	14	76	-71
-2	15	16	-11
-2	16	12	-16
-3	1	56	60
-3	2	216	-221
-3	3	13	21
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-3	6	75	82
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-3	8	20	-18
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-4	12	38	-31
-4	13	50	49
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-5	4	39	-44
-5	5	21	14
-5	6	151	139
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-5	8	30	31
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-5	11	5	11
-5	12	30	-32
-6	1	34	-31
-6	2	6	23
-6	3	6	5
-6	4	45	-47
-6	5	27	29
-6	6	141	-138
-6	7	38	34
-6	8	21	17
-6	9	6	0
-6	10	5	3
-7	1	122	120
-7	2	32	31
-7	3	5	-20
-7	4	29	31
-7	5	27	-33
-7	6	61	68
-7	7	18	24
-7	8	4	-10
-7	9	71	-56
-7	10	36	-32
-8	1	5	0
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-8	3	55	-59
-8	4	5	10
-8	5	12	-16
-8	6	18	-18
L = 4			
0	0	48	53
0	1	56	64
0	2	33	-33
0	3	192	242
0	4	19	17
0	5	60	58
0	6	116	98
0	7	15	24
0	8	17	-19
0	9	50	51
0	10	46	-45
0	11	89	-79
0	12	4	-7
0	13	4	9
0	14	12	-14
0	15	21	23
1	0	231	-235
1	1	35	34
1	2	4	-4
1	3	187	-181
1	4	260	279
1	5	180	-174
1	6	38	38
1	7	23	22
1	8	81	-113
1	9	45	40
1	10	21	-17
1	11	55	43
1	12	4	-8
2	0	144	-132
2	1	44	-35
2	2	17	18
2	3	46	35
2	4	4	8
2	5	81	61
2	6	62	-51
2	7	52	-43
2	8	31	-28
2	9	56	-44
2	10	4	-4
2	11	14	-25
2	12	60	55
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3	2	65	-53
3	3	12	-12
3	4	128	107
3	5	57	47
3	6	66	55
3	7	101	82
3	8	89	-69
3	9	20	23
4	0	17	-20
4	1	4	8
4	2	39	30
4	3	17	-18
4	4	22	22
5	0	17	0
5	1	14	0
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-1	1	65	56
-1	2	37	-35
-1	3	23	-26
-1	4	15	21
-1	5	17	-2
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-1	12	90	86
-1	13	46	-41
-1	14	66	57
-2	0	275	330
-2	1	58	-51
-2	2	24	-23
-2	3	151	-140
-2	4	66	-66
-2	5	126	-108
-2	6	33	-21
-2	7	23	18
-2	8	4	4
-2	9	46	-45
-2	10	52	50
-2	11	57	-60
-2	12	69	-67
-2	13	33	29
-2	14	3	4
-2	15	22	23
-3	0	69	-63
-3	1	122	-122
-3	2	13	16
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-3	6	173	157
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-3	9	65	60
-3	10	105	-97
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-3	12	4	5
-3	13	4	6
-3	14	27	-52
-3	15	21	-20
-4	0	31	33
-4	1	78	-89
-4	2	3	6
-4	3	110	-118
-4	4	74	-68
-4	5	231	231
-4	6	157	-161
-4	7	121	133
-4	8	4	-9
-4	9	127	-127
-4	10	79	74
-4	11	35	-32
-4	12	20	13
-4	13	24	-23
-4	14	56	41
-4	15	17	19
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-5	2	45	-40
-5	3	109	-110
-5	4	93	101
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-5	7	4	-14
-5	8	38	-35
-5	9	45	41
-5	10	39	32
-5	11	33	-31
-5	12	4	-9
-5	13	28	22
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-6	1	46	-42
-6	2	79	77
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-6	4	50	46
-6	5	72	75
-6	6	4	-3
-6	7	62	62
-6	8	28	-24
-6	9	20	-16
-6	10	52	-42
-6	11	33	-30
-6	12	25	16
-7	0	80	-75
-7	1	71	69
-7	2	48	-44
-7	3	75	71
-7	4	42	37
-7	5	4	-4
-8	0	40	40
-8	1	4	-6
-8	2	4	11
-8	3	41	-32
-8	4	38	-35
-8	5	86	-68
L = 5			
0	1	250	-334
0	2	24	31
0	3	122	137
0	4	41	39
0	5	112	106
0	6	7	-2
0	7	25	31
0	8	57	-43
0	9	6	-8
0	10	6	26
0	11	6	11
1	1	76	76
1	2	59	-64
1	3	6	-5
1	4	44	46
1	5	28	26
1	6	6	9
1	7	54	-54
1	8	28	27
1	9	69	-64
1	10	43	42
2	1	57	-51
2	2	6	10
2	3	69	66
2	4	53	-50
2	5	84	79
2	6	5	23
-1	1	72	82
-1	2	113	111
-1	3	5	13
-1	4	83	-94
-1	5	6	16
-1	6	54	-56
-1	7	93	-109
-1	8	6	-21
-1	9	6	-1
-1	10	57	-54
-2	3	88	79
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-2	8	39	40
-2	9	88	-92
-2	10	76	87
-2	11	6	-8
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-3	2	5	4
-3	3	24	-29
-3	4	93	-92
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-3	6	88	89
-3	7	6	19
-3	8	38	41
-3	9	76	85
-3	10	6	14
-4	1	5	3
-4	2	71	66
-4	3	100	-105
-4	5	82	95
-4	6	54	-73
-4	7	31	38
-4	8	6	-11
-4	9	6	-23
-4	10	76	-76
-5	1	117	120
-5	2	239	-242
-5	3	43	46
-6	1	121	-119
-6	2	36	32
-6	3	6	6
-7	1	34	-31
-7	2	87	-99
-7	3	6	3
L = 6			
0	0	34	32
0	1	5	4
0	2	53	-45
0	3	84	-88
0	4	5	-4
0	5	79	-74
0	6	74	69
1	0	125	-119
1	1	6	11
1	2	6	-2
1	3	35	33
1	4	34	29
2	0	98	114
2	1	5	3
-1	0	59	-64
-1	2	5	16
-1	3	161	159
-2	0	82	-91
-2	1	38	31
-2	2	49	35
-2	3	25	-41
-2	4	6	-15
-3	1	59	60
-3	2	78	-67
-4	1	54	-63
-4	2	67	71
-4	3	29	-21
-5	1	117	130
-5	3	68	57
-6	1	84	-103
-6	2	47	-76
-7	2	33	47
L = 7			
-1	2	62	62
-2	2	48	47
-3	2	67	-66
-4	2	93	102

Least-squares refinement was carried out using a full matrix program for the IBM 704 by Busing & Levy (1959). The Hughes (1941) weighting scheme was used and the unobserved reflexions were omitted. Two isotropic and two anisotropic cycles were computed. The second anisotropic calculation included the hydrogen atoms at positions determined from a difference synthesis the coordinates of which were not refined.

Table 2. *Fractional atomic coordinates and atomic anisotropic thermal parameters*

Atom	x	y	z
C_2	−0·5242	0·0744	−0·2965
C_4	−0·1316	0·1116	−0·0845
C_5	−0·1341	0·1468	−0·3102
C_6	−0·3594	0·1602	−0·5163
N_1	−0·5330	0·1182	−0·4950
N_3	−0·3214	0·0735	−0·0969
O_2	−0·6871	0·0383	−0·2951
O_4	0·0357	0·1135	0·1090
O_6	−0·3885	0·2007	−0·6953
H_1	−0·663	0·138	−0·600
H_3	−0·330	0·025	−0·007
H_5'	−0·077	0·090	−0·367
H_5	−0·043	0·206	−0·267

Atom	B_{11} (Å^2)	B_{22} (Å^2)	B_{33} (Å^2)	B_{12} (Å^2)	B_{13} (Å^2)	B_{23} (Å^2)
C_2	2·17	2·90	1·42	0·11	0·68	0·07
C_4	2·23	3·61	2·10	0·16	0·55	0·00
C_5	2·00	4·22	2·50	0·07	1·12	0·24
C_6	2·70	2·70	2·28	−0·20	1·12	−0·06
N_1	2·25	2·90	1·40	−0·02	0·81	0·24
N_3	2·00	3·75	1·97	−0·21	0·19	0·12
O_2	2·21	4·00	2·40	−0·08	0·81	0·60
O_4	2·00	0·40	2·63	0·00	−0·47	0·46
O_6	4·02	4·62	2·71	−0·53	1·48	0·83

A final structure factor calculation gave an agreement index of 10·2% for the observed reflexions only and 10·4% when unobserved reflexions were included at half the observable minimum. The results from this are shown in Table 1. The final atomic coordinates and anisotropic thermal parameters are given in Table 2. The mean estimated standard deviations were $\sigma(x)=0·004$ Å, $\sigma(y)=0·004$ Å, and $\sigma(z)=0·005$ Å, for the positional parameters of the C, N and O atoms. For the thermal parameters the mean standard deviations were $\sigma(B_{11})=0·16$, $\sigma(B_{22})=0·20$, $\sigma(B_{33})=0·20$, $\sigma(B_{12})=0·12$, $\sigma(B_{13})=0·13$ and $\sigma(B_{23})=0·13$ Å^2.

The hydrogen atom positions

At the completion of the first anisotropic refinement cycle, the bond lengths indicated clearly that the molecule was in the tri-keto form I. There were however, three intermolecular distances less than 3·0 Å which might be associated with hydrogen-bonding and it was desirable to locate the hydrogen atoms directly if the data permitted. The three-dimensional difference Fourier computed at this stage of the analysis where $R=0·109$, is shown as a composite projection in Fig. 5. The four largest peaks corresponded to the hydrogen atoms, at positions in agreement with the tri-keto tautomeric formula.

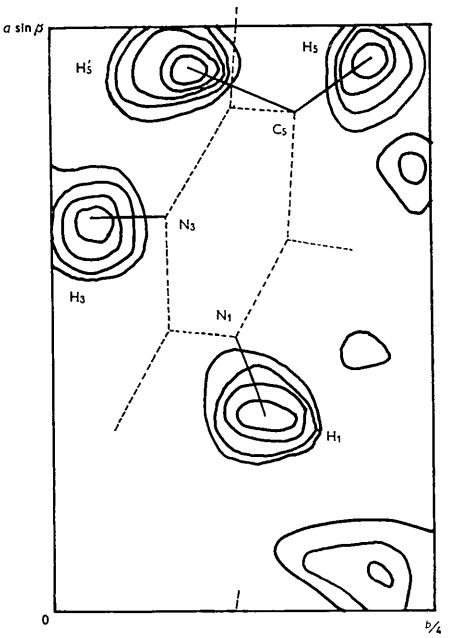
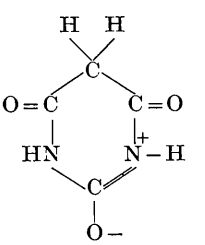


Fig. 5. The composite projection of the three-dimensional difference Fourier showing hydrogen atoms. Contours are at 0·2 e.Å with the zero contour omitted.

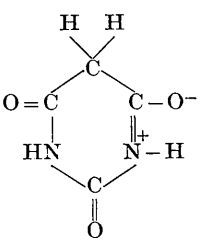
The hydrogen atom parameters given in Table 2 were deduced from this difference synthesis. The mean standard deviations of the coordinates are $\sigma(r)=0·06$ Å.

Discussion of the structure

The bond lengths and bond angles in the barbituric acid molecule are given in Table 3. They correspond to the tri-keto tautomer, I, with resonance contributions from valence-bond forms of the type VI and VII.



VI



VII

These values are compared with those found in the dihydrate structure in Fig. 6. The differences are not significant. In the two structures, the observed C–N bond lengths vary from 1·35 to 1·39 with a mean value

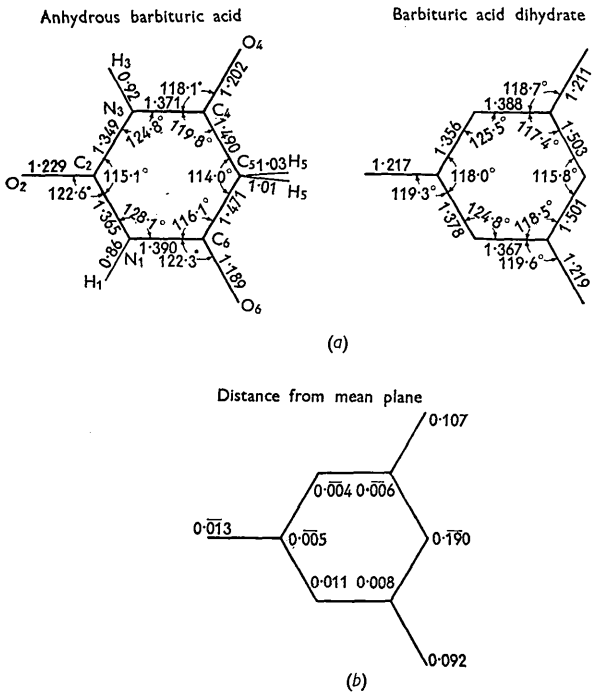


Fig. 6. (*a*) The dimensions of a barbituric acid molecule in the anhydrous compound and the dihydrate. (*b*) Displacements from the mean molecular plane in the anhydrous crystal.

Table 3. *Molecular dimensions and planarity*

Bond	Length	$\sigma(AB)$	Angles		$\sigma(ABC)$
C_4–C_5	1·490 Å	0·007 Å	C_4–C_5–C_6	114·0°	0·4°
C_6–C_5	1·471	0·007	C_5–C_6–N_1	116·1	0·4
C_4–N_3	1·371	0·006	C_6–N_1–C_2	128·1	0·4
C_6–N_1	1·390	0·006	N_1–C_2–N_3	115·1	0·4
N_3–C_2	1·349	0·006	C_2–N_3–C_4	124·8	0·4
N_1–C_2	1·365	0·006	N_3–C_4–C_5	119·8	0·5
C_2–O_2	1·229	0·006	N_3–C_4–O_4	118·1	0·5
C_4–O_4	1·202	0·006	N_1–C_6–O_6	122·3	0·5
C_6–O_6	1·189	0·006	N_1–C_2–O_2	122·6	0·4
			N_3–C_2–O_2	121·4	0·4
C_5–H_5'	1·03		C_5–C_4–O_4	121·4	0·5
C_5–H_5	1·01		C_5–C_6–O_6	121·5	0·5
N_3–H_3	0·92				
N_1–H_1	0·86				

Equation to the plane:

(1) $-0{\cdot}3974X+0{\cdot}8674Y+0{\cdot}4529Z-1{\cdot}5053=0$
(2) $-0{\cdot}3953X+0{\cdot}8702Y+0{\cdot}4455Z-1{\cdot}5180=0$

Deviations from plane (1)		Δ/σ	Deviations from plane (2)	Δ/σ
C_2	0·000 Å	0·0	−0·005 Å	1·1
C_4	0·002	0·4	−0·006	1·1
C_5	0·198*	39·6	−0·190	38·0
C_6	0·003	0·6	0·008	1·6
N_1	0·005	1·5	0·011	1·0
N_3	0·004	1·0	−0·004	1·0
O_2	0·004	1·2	−0·013	3·8
O_4	0·115*	28·1	0·107	26·3
O_6	0·072*	18·0	0·092	22·5

* Omitted from L.S. calculation.

of 1·37 Å. This corresponds to 23% double-bond character using Pauling's (1960) equation with a C–N single bond = 1.43 Å and a C=N$^+$ double bond = 1·26 Å. The C–C bond lengths are between 1·47 and 1·50 Å, with a mean of 1·491 Å, for the sp^3–sp^2 bonds which must be close to pure single bond in character. One of the C–O bonds is noticeably shorter than the others and since this is the only carbonyl group which is not involved in a hydrogen bond this may be a significant observation. However, in general, any differences in the electronic structure of the molecules, as a consequence of their different crystal environments in the anhydrous and hydrated forms, are so small that they cannot be detected from these bond length measurements, with maximum standard deviations of 0·01 Å.

Table 4. *The intermolecular distances less than* 4·0 Å

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

Distances (Å)

C_2 (II)	$-C_2$ (X)	3·45	C_6 (III)	$-O_6$ (VIII)	3·87
C_2 (II)	$-C_6$ (X)	3·52	C_5 (III)	$-O_6$ (I)	3·08
C_2 (I)	$-O_6$ (VI)	3·86	C_5 (I)	$-O_2$ (V)	3·38
C_2 (II)	$-O_6$ (X)	3·98	C_5 (II)	$-O_2$ (X)	3·42
C_2 (III)	$-O_6$ (I)	3·33	C_5 (II)	$-O_4$ (I)	3·89
C_2 (II)	$-O_2$ (VII)	3·64	C_5 (III)	$-O_4$ (VIII)	3·73
C_2 (II)	$-O_2$ (X)	3·83	O_6 (III)	$-O_6$ (I)	3·43
C_2 (I)	$-O_4$ (X)	3·53	O_6 (II)	$-O_2$ (X)	3·46
C_2 (II)	$-N_3$ (VII)	3·76	O_6 (I)	$-O_4$ (VI)	3·85
C_2 (II)	$-N_1$ (X)	3·15	O_6 (I)	$-O_4$ (IX)	3·73
C_4 (II)	$-C_4$ (I)	3·57	O_6 (III)	$-O_4$ (I)	3·71
C_4 (III)	$-C_6$ (I)	3·73	O_6 (I)	$-N_3$ (VI)	3·30
C_4 (III)	$-C_5$ (I)	3·86	O_6 (III)	$-N_3$ (I)	3·28
C_4 (I)	$-O_6$ (VI)	3·83	O_6 (III)	$-N_1$ (I)	3·07
C_4 (III)	$-O_6$ (I)	3·10	O_2 (II)	$-O_2$ (VII)	3·51
C_4 (I)	$-O_2$ (V)	3·98	O_2 (I)	$-O_4$ (VII)	3·96
C_4 (II)	$-O_2$ (VII)	3·82	O_2 (I)	$-O_4$ (X)	3·45
C_4 (II)	$-O_4$ (I)	3·30	O_2 (II)	$-O_4$ (VII)	3·79
C_4 (II)	$-N_3$ (I)	3·81	O_2 (II)	$-N_1$ (X)	3·30
C_4 (I)	$-N_1$ (IX)	3·98	O_4 (II)	$-O_4$ (I)	3·46
C_6 (III)	$-O_6$ (I)	2·90	O_4 (II)	$-N_3$ (I)	3·33
C_6 (II)	$-O_2$ (X)	3·15	N_3 (II)	$-N_3$ (VII)	3·83
C_6 (I)	$-O_4$ (X)	3·70	N_3 (II)	$-N_1$ (X)	3·55
C_6 (I)	$-N_3$ (VIII)	3·96	N_1 (II)	$-N_1$ (X)	3·42
O_2 (II)	$-N_3$ (VII)	2·90			
O_2 (II)	$-H_3$ (VII)	2·02			
O_4 (I)	$-N_1$ (IX)	2·80			
O_4 (I)	$-H_1$ (IX)	2·02			

There is a significant deviation from planarity in the molecule in the anhydrous crystal, as shown in Table 3 and Fig. 6(*b*). This is such as to increase the $C_5 \cdots O_6$ intermolecular distance to 3·08 Å, from a value of about 2·8 Å if these atoms were in the plane of the ring. There are no apparent intermolecular interactions associated with the displacement of O_4. However, the displacements of C_5, O_6 and O_4 taken together give the methylene half of the ring a boat-shaped configuration which is more compatible with

a tetrahedral angle and the sp^3 bonding orbitals of the methylene carbon atom.

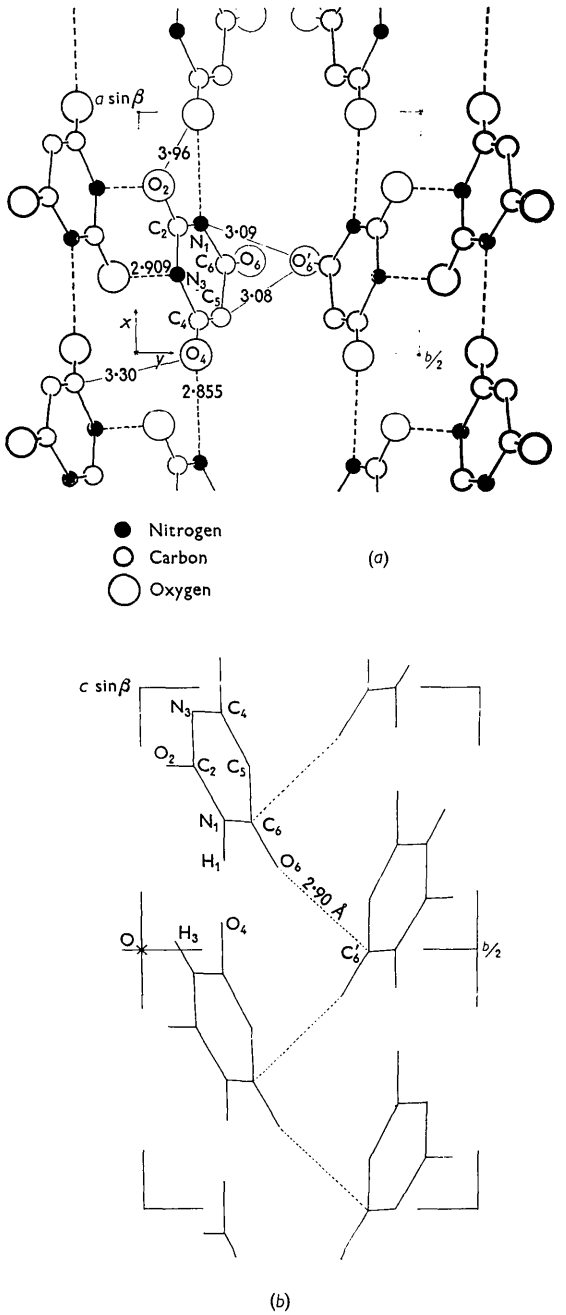


Fig. 7. The structure of anhydrous barbituric acid. (*a*) Projected on (001); hydrogen bonds are shown as broken lines. (*b*) Projected on (100); broken lines show the close C · · · O approaches.

The intermolecular separations less than 4.0 Å are shown in Table 4 and Fig. 7. There are three distances less than 3·0 Å. Two of these, $O_2 \cdots N_3$ at 2·90 Å and $O_4 \cdots N_1$ at 2·80 Å, correspond to hydrogen bonds, since the hydrogen atoms lie approximately on the line of centers of the heavier atoms. Although these distances differ by 0·1 Å, it is interesting to note that the oxygen to hydrogen distances are equal at 2·02 Å. These bonds link the molecules in infinite ribbons, two molecules wide, parallel to the *a* axis. The perpendicular distance between parallel ribbons is 3·03 Å, and the closest approach between any pair of atoms in them is 3·15 Å.

The third carbonyl oxygen, O_6, is not involved in hydrogen-bonding although it approaches close, at 2·90 Å, to the same carbonyl carbon atom of an adjacent molecule. This structure provides an unusual example of two equal intermolecular separations, one of which is clearly a hydrogen bond while the other is not. The methylene carbon atom C_5 is only 3·08 Å away from O_6 in an adjacent molecule but there is no C–H · · · O type interaction as the closest hydrogen approach to O_6 is 2·62 Å. Short intermolecular distances involving the oxygen of a nitro group and methylene carbon atoms, of 3·01 Å and 3·12 Å have also been observed in cyclotetramethylene tetranitramine by Eiland & Pepinsky (1955). They concluded, also that the methylene hydrogen atoms were most probably not directly involved in the close approaches, being at 2·41 Å from the oxygen atom.

In this structure, in parabanic acid (Davies & Blum, 1955) and in chloranil (Chu, Jeffrey & Sakurai, 1962), the non-hydrogen bonding intermolecular distances less than 3·0 Å all involve carbonyl atoms only, and there is a marked similarity in the orientation of these groups. In all three structures the direction of the interaction is such that the σ bond direction of the carbonyl group is approximately collinear with the polar axis of the bond at the carbon atom, (cf. Fig. 7(*b*) in this paper with Fig. 5 in Chu, Jeffrey & Sakurai, 1962).

While it has not been observed as a general rule that carbonyl groups are involved in intermolecular separations less than the sum of the usual van der Waals radii, *cf.* benzoquinone (Trotter, 1960), succinimide (Mason, 1956), there are now these cases where it does occur. Presumably this is connected with the strong dipolar nature of the C=O group, which permits a close approach between molecules, provided this is compatible with other aspects of the intermolecular packing or of the hydrogen bonding.

APPENDIX

In order to use the Taylor & Morley (1959) method of molecule location it was necessary to derive a structure factor expression in terms of the coordinates of the centre of the molecule and the value of the Fourier transform at the reciprocal lattice point. For the plane group *pg* this was done in the following way.

A molecule whose atoms are at (x_n, y_n) with respect to the molecular centre (X, Y) will contribute to an $(hk0)$ structure factor:

$$= \sum_n f_n \exp 2\pi i(h(X+x_n)+k(Y+y_n))$$
$$= [\sum_n f_n \exp 2\pi i(hx_n+ky_n)] \exp 2\pi i(hX+kY)$$
$$= G_0 \exp 2\pi i(hX+kY) .$$

The contribution of a space group related molecule centered at $(\overline{X}\,\overline{Y})$ is:

$$= G_0^* \exp 2\pi i(h\overline{X}+k\overline{Y}) ,$$

where G_0^* is the complex conjugate of G_0, the value of the Fourier transform of a single molecule at the reciprocal lattice point $(hk0)$.

The total contribution of these two molecules to $F(hk0)$ is:

$$\begin{aligned} &= G_0 \exp 2\pi i(hX+kY)+G_0^* \exp 2\pi i(hX+kY) \\ &= (A+iB)[\cos 2\pi(hX+kY)+i \sin 2\pi(hX+kY)] \\ &+ (A-iB)[\cos 2\pi(hX+kY)-i \sin 2\pi(hX+kY)] \\ &= 2A \cos 2\pi(hX+kY)-2B \sin 2\pi(hX+kY) \qquad (1) \end{aligned}$$

where A and B are the real and complex parts of G_0.

In a similar way, the contributions of space group related molecules centred at $(X, \frac{1}{2}-Y)$, $(\overline{X}, \frac{1}{2}+Y)$ is:

$$\begin{aligned} &G_1[\cos 2\pi(hX+k(\tfrac{1}{2}-Y))+i \sin 2\pi(hX+k(\tfrac{1}{2}-Y))] \\ &+G_1^*[\cos 2\pi(h\overline{X}+k(\tfrac{1}{2}+Y))+i \sin 2\pi(h\overline{X}+k(\tfrac{1}{2}+Y))] \end{aligned}$$

where (2)

$$G_1 = A_1+iB_1 = \sum_n f_n \exp 2\pi i(hx_n-ky_n) .$$

The real and complex parts of G_1 at $(hk0)$ are the real and complex parts of the transform at the lattice point $(hk0)$. The values of A, B, A_1 and B_1 could therefore be obtained by placing the calculated plane transform of a single molecule over the $(hk0)$ reciprocal lattice net in the best transform fit orientation, and reading off the values of its real and complex parts at $(hk0)$ and $(h\bar{k}0)$.

For an $(h00)$ structure factor the sum of (1) and (2) simplified to:

$$F_G(h00) = 2(A+A_1) \cos 2\pi hX-2(B+B_1) \sin 2\pi hX$$

and for an $(0k0)$ reflexion

$$F_G(0k0) = 2(A+A_1) \cos 2\pi kY-2(B-B_1) \sin 2\pi kY .$$

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