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The Crystal Structure of Anhydrous Dilituric Acid

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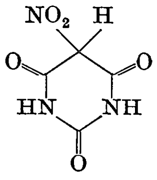
The crystal structure of dilituric acid (5-nitrobarbituric acid) has been determined by the three-dimensional Fourier transform method and refined by least squares with anisotropic temperature factors.

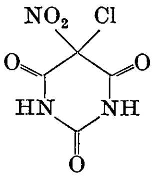
The molecule is in the 5-nitro-2,6-dioxo-4-hydroxy configuration and not the commonly reported trioxo form. There is an intramolecular hydrogen bond of 2·497 Å in the molecule and the C–NO_2 bond is rather short at 1·407 Å.

Introduction

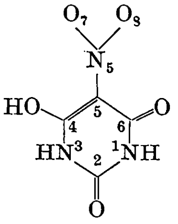
Dilituric acid is the 5-nitro derivative of barbituric acid. Its configurational formula is generally written as (I) because this best describes its chemical behaviour, particularly the ready formation of 5-derivatives such as (II). The trioxo configuration is also suggested by analogy with barbituric acid (Jeffrey, Ghose & Warwicker, 1961). However there are six alternative tautomeric formulae of which (III), with the nitro group coplanar with the pyrimidine ring, is not unlikely.



(I)



(II)



(III)

The compound is of interest in analytical chemistry. It forms characteristic crystalline derivatives with amino acids and aromatic amines and is used as a gravimetric agent for nickel and copper. It is unusual in forming an almost insoluble potassium salt.

The common crystalline form of dilituric acid is a trihydrate (Baeyer, 1880). In this there are at least eight hydrogens available for hydrogen bonding with ten nitrogen and oxygen atoms. Crystals of the anhydrous compound on the other hand have only two protons to share between seven such atoms. Therefore, unless bifurcated hydrogen bonds are formed, some oxygen atoms will not be hydrogen-bonded. In parabanic acid (Davies & Blum, 1955), chloranil (Chu, Jeffrey & Sakurai, 1962) and anhydrous barbituric acid (Bolton, 1962) where there is a similar deficiency of hydrogen atoms, close intermolecular contacts between carbonyl oxygen atoms and carbon atoms of C=O bonds are observed. These are of the order of 2·8 Å and the direction of interaction is approximately the same in all the cases. In view of the deficiency of hydrogen atoms for hydrogen bonding in anhydrous dilituric acid, the intermolecular association was considered to be of particular interest. The structure was examined as as part of a general investigation of the crystal structures of pyrimidine derivatives which are proton-deficient for the hydrogen bonding of all the electronegative substituents.

Experimental

As there are no crystal data in the literature relating to dilituric acid, particulars of two hydrates, which were prepared incidentally, are reported here, together with the data for the anhydrous crystals. Crystallization from water gives two polymorphic forms of the trihydrate. At room temperature small tabular crystals* are obtained. These are stable in air and have monoclinic symmetry with:

$$a=20{\cdot}97,\ b=6{\cdot}40,\ c=12{\cdot}24\ \text{Å};\ \beta=110{\cdot}5^\circ;$$
$$D_m=1{\cdot}682,\ D_x=1{\cdot}664\ \text{g.cm}^{-3};$$
$$Z=8\,(C_4H_3O_5N_3\,.\,3\,H_2O)\,.$$

Systematic absences $0k0$ for k and $h0l$ for l odd indicate the space group $P2_1/c$.

Slow evaporation of an aqueous solution at about 55 °C gives tabular crystals of a triclinic modification. These are unstable and lose water to the air at room temperature. The crystal data for this form are:

$$a=12{\cdot}00,\ b=7{\cdot}64,\ c=10{\cdot}33\ \text{Å};$$
$$\alpha=90^\circ,\ \beta=115^\circ,\ \gamma=88^\circ;$$
$$D_m=1{\cdot}750,\ D_x=1{\cdot}743\ \text{g.cm}^{-3};$$
$$Z=4\,(C_4H_3O_5N_3\,.\,3\,H_2O)\,.$$

The space group is $P1$ or $P\bar{1}$.

These unit-cell dimensions were measured from

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* Further structural work on this compound is in progress.

rotation and Weissenberg photographs and are subject to errors of about 1% and 1° respectively.

Crystals of a monohydrate, which was shown to be a phase in the dilituric acid–H_2O system by Loeffler & Moore (1948) from vapour pressure studies, could not be isolated from water or slightly wet ethanolic solutions.

Small crystals of anhydrous dilituric acid were obtained by slowly evaporating a solution in dry ethanol saturated at its boiling point. These were short prisms of indeterminate habit, slightly elongated about the *b* axis. The crystals used in this analysis were 0·3 × 0·4 × 0·2 mm.

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

$$a = 8{\cdot}937 \pm 0{\cdot}005,\ b = 6{\cdot}262 \pm 0{\cdot}003,$$
$$c = 11{\cdot}875 \pm 0{\cdot}005\ \text{Å};\ \beta = 112°\ 11' \pm 6'.$$

From the systematic extinctions $0k0$ absent with k odd, $h0l$ absent with l odd, the space group is $P2_1/c$, $Z = 4$, $D_x = 1{\cdot}872$ g.cm^{-3} and $D_m = 1{\cdot}874$ g.cm^{-3}.

Intensities were recorded on multiple-film Weissenberg photographs with Cu $K\alpha$ radiation. A complete set of equi-inclination photographs about the *a* and *b* axes, with μ up to 35° were obtained. These were measured by visual comparison with a calibrated intensity scale. In order to reduce the correlation errors, the *hkl* intensities obtained from the *b*-axis photographs were correlated from double-layer photographs, as described by Stadler (1950), before scaling and averaging with the *hkl* intensities from the *a*-axis photographs. Out of a possible total of 1500 reflections within the reflecting sphere 1220 were recorded, of which 200 were too weak to measure. No corrections were applied for the small absorption errors.

The structure determination

The orientation of the single molecule in the asymmetric unit was found by fitting the highest peaks of the three-dimensional Fourier transform against the weighted reciprocal lattice. For this purpose the Fourier transform of barbituric acid (Bolton, 1963) was used as it was expected to differ only in detail from the nitrobarbituric acid transform and was available from earlier work.

It was not possible to fit the transform satis-

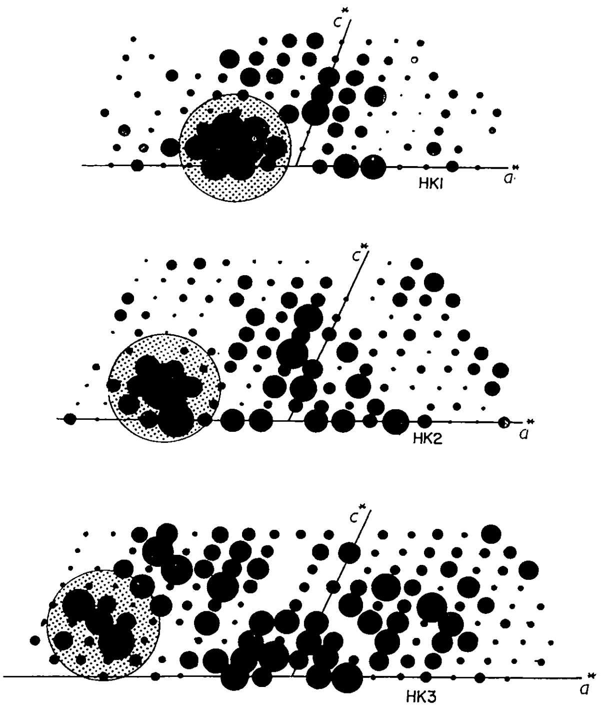

Fig. 1. Part of the weighted reciprocal lattice of dilituric acid showing the transform origin peaks.

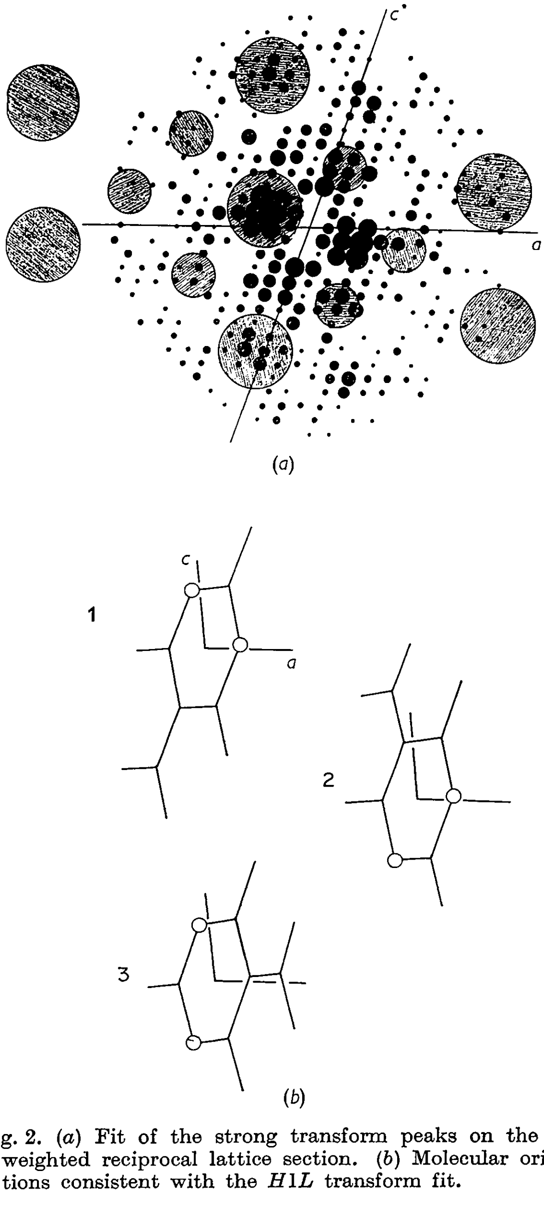

Fig. 2. (*a*) Fit of the strong transform peaks on the *H*1*L* weighted reciprocal lattice section. (*b*) Molecular orientations consistent with the *H*1*L* transform fit.

factorily against the *H0L* weighted reciprocal lattice section because of the poor resolution in the (010) projection. The *H1L*, *H2L* and *H3L* weighted reciprocal lattice sections were therefore examined to locate the transform origin peaks (Stadler, 1960). These were easily discernible on each section as regions of high scattering lying on a straight line through the origin. This is shown in Fig. 1. From the position of the origin peaks the orientation of the molecular plane was deduced, and hence it was possible to construct

Table 1. *Observed and calculated structure factors*

		FOBS	FCAL
K=	0		
0	2	445	-526
0	4	171	-191
0	6	201	197
0	8	215	-213
0	10	119	100
0	12	180	179
0	14	175	181
1	0	34	16
1	2	55	64
1	4	84	88
1	6	160	179
1	8	73	-71
1	10	72	66
1	12	180	174
2	0	661	-750
2	2	473	-497
2	4	501	-525
2	6	257	271
2	8	41	40
2	10	114	109
2	12	29	17
3	0	75	65
3	2	487	-572
3	4	50	-60
3	6	66	-66
3	8	11	-16
3	10	75	-73
4	0	306	-320
4	2	89	-93
4	4	473	513
4	6	69	-62
4	8	143	-148
4	10	6	5
5	0	208	222
5	2	55	57
5	4	30	-27
5	6	107	118
5	8	94	91
6	0	52	-43
6	2	61	56
6	4	62	59
6	6	61	-64
6	8	30	34
7	0	61	-65
7	2	44	33
7	4	15	-16
7	6	77	78
8	0	16	12
8	2	79	-78
-1	2	501	522
-1	4	32	30
-1	6	105	-90
-1	8	11	-1
-1	10	125	-116
-1	12	79	-88
-1	14	11	1
-2	2	517	546
-2	4	169	-159
-2	6	187	188
-2	8	107	128
-2	10	751	-832
-2	12	115	118
-2	14	40	-33
-3	2	55	40
-3	4	384	-450
-3	6	6	2
-3	8	89	91
-3	10	55	58
-3	12	139	-138
-3	14	54	49
-4	2	147	148
-4	4	361	-300
-4	6	243	254
-4	8	235	247
-4	10	341	391
-4	12	175	-194
-4	14	61	55
-5	2	77	-67
-5	4	228	236
-5	6	26	14
-5	8	199	234
-5	10	84	-96
-5	12	59	47
-5	14	130	108
-6	2	258	266
-6	4	48	39
-6	6	501	-500
-6	8	133	112
-6	10	44	40
-6	12	64	-57
-6	14	82	58
-7	2	171	-153
-7	4	150	-134
-7	6	66	55
-7	8	161	-140
-7	10	13	6
-7	12	13	3
-7	14	193	-176
-8	2	62	-69
-8	4	16	13
-8	6	13	-10
-8	8	41	-38
-8	10	16	10
-8	12	66	-66
-9	2	179	215
-9	4	86	-89
-9	6	66	-41
-9	8	13	-8
-9	10	50	54
-9	12	64	78
K=	1		
0	1	62	67
0	2	29	26
0	3	487	-535
0	4	375	-382
0	5	299	-294
0	6	100	81
0	7	54	55
0	8	135	-150
0	9	203	-199
0	10	253	283
0	11	26	28
0	12	75	-80
0	13	25	26
1	0	224	-215
1	1	197	185
1	2	229	-252
1	3	250	-231
1	4	250	-244
1	5	295	332
1	6	204	188
1	7	58	-51
1	8	236	245
1	9	342	-390
1	10	114	-112
1	11	11	1
1	12	30	31
1	13	76	-45
2	0	793	-1028
2	1	69	-67
2	2	171	175
2	3	72	-62
2	4	314	304
2	5	129	137
2	6	153	-157
2	7	52	40
2	8	126	116
2	9	58	59
2	10	12	21
2	11	12	-19
2	12	61	-52
3	0	473	500
3	1	22	-17
3	2	23	-17
3	3	41	32
3	4	16	-22
3	5	66	77
3	6	104	107
3	7	86	-92
3	8	9	6
3	9	128	130
3	10	87	-88
3	11	126	97
4	0	45	41
4	1	82	-88
4	2	6	8
4	3	6	-15
4	4	77	77
4	5	137	140
4	6	43	-35
4	7	8	16
4	8	27	25
4	9	52	-43
4	10	101	-92
4	11	43	56
5	0	59	47
5	1	226	-235
5	2	130	149
5	3	111	-126
5	4	115	-126
5	5	9	-3
5	6	48	42
5	7	70	77
5	8	89	-91
5	9	47	-44
6	0	168	211
6	1	83	-94
6	2	6	4
6	3	61	54
6	4	87	-94
6	5	36	-25
6	6	57	51
6	7	94	-91
6	8	19	-19
7	0	48	-49
7	1	37	35
7	2	89	-91
7	3	128	133
7	4	70	66
7	5	13	21
7	6	13	-13
7	7	89	-61
8	0	37	42
8	1	54	55
8	2	13	-4
8	3	91	-80
8	4	73	-65
8	5	48	40
9	1	37	-11
9	2	144	-114
9	3	70	-54
9	4	116	84
10	0	83	-61
10	1	158	-118
-1	1	348	-310
-1	2	59	-58
-1	3	403	-455
-1	4	139	-126
-1	5	70	-58
-1	6	238	-243
-1	7	290	290
-1	8	87	-81
-1	9	206	206
-1	10	112	106
-1	11	66	-59
-1	12	77	66
-1	13	87	69
-1	14	58	49
-2	1	626	729
-2	2	501	-508
-2	3	40	42
-2	4	168	185
-2	5	278	282
-2	6	153	-162
-2	7	222	222
-2	8	34	32
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-2	10	112	-123
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-3	4	171	161
-3	5	338	-380
-3	6	200	-200
-3	7	171	172
-3	8	26	-14
-3	9	93	-106
-3	10	69	-63
-3	11	34	26
-3	12	19	-18
-3	13	104	102
-3	14	15	19
-4	1	260	-293
-4	2	171	185
-4	3	48	54
-4	4	123	-132
-4	5	165	-170
-4	6	306	318
-4	7	19	-9
-4	8	19	-25
-4	9	87	97
-4	10	200	-217
-4	11	215	-248
-4	12	125	137
-4	13	75	-85
-4	14	97	-93
-5	1	278	-277
-5	2	47	-46
-5	3	80	70
-5	4	91	91
-5	5	55	-56
-5	6	6	-9
-5	7	47	-38
-5	8	72	69
-5	9	30	37
-5	10	143	152
-5	11	250	-264
-5	12	250	-259
-5	13	58	-49
-5	14	36	35
-6	1	153	151
-6	2	76	78
-6	3	61	-51
-6	4	34	31
-6	5	187	-198
-6	6	34	-23
-6	7	34	26
-6	8	6	7
-6	9	70	68
-6	10	82	77
-6	11	151	170
-6	12	93	-93
-6	13	30	-19
-6	14	44	44
-7	1	80	75
-7	2	190	-210
-7	3	34	-29
-7	4	84	97
-7	5	12	17
-7	6	76	-78
-7	7	44	34
-7	8	70	77
-7	9	121	122
-7	10	37	-26
-7	11	137	157
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-7	13	33	-26
-7	14	62	-56
-8	1	33	20
-8	2	13	-6
-8	3	132	131
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-8	5	64	61
-8	6	83	-78
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-8	10	89	106
-8	11	111	-113
-8	12	34	-41
-8	13	61	43
-9	1	11	-7
-9	2	37	-32
-9	3	76	77
-9	4	11	-22
-9	5	37	-33
-9	6	54	78
-9	7	93	-90
-9	8	107	-123
-9	9	37	-26
-9	10	33	29
-9	11	70	-62
-9	12	165	98
-10	1	9	2
-10	2	12	-14
-10	3	72	-66
-10	4	12	-10
-10	5	37	-42
-10	6	37	-47
-10	7	87	90
-10	8	12	-2
-10	9	47	-45
-10	10	12	-11
-11	4	52	-42
-11	5	11	-25
-11	6	76	61
-11	7	54	38
-11	8	107	-92
K=	2		
0	0	11	11
0	1	175	166
0	2	388	440
0	3	277	304
0	4	54	35
0	5	167	-157
0	6	93	81
0	7	54	52
0	8	8	-5
0	9	45	-32
0	10	164	164
0	11	45	-41
0	12	82	58
1	0	325	368
1	1	215	-183
1	2	144	-132
1	3	9	1
1	4	271	247
1	5	104	-89
1	6	254	264
1	7	23	17
1	8	77	75
1	9	36	44
1	10	115	-92
1	11	55	-62
1	12	52	46
2	0	324	-333
2	1	70	57
2	2	348	-359
2	3	144	-131
2	4	72	56
2	5	75	-70
2	6	40	24
2	7	141	-125
2	8	141	150
2	9	133	138
2	10	157	-182
2	11	22	-27
2	12	20	24
3	0	140	144
3	1	210	205
3	2	72	-53
3	3	15	-11
3	4	82	-70
3	5	98	-86
3	6	68	-50
3	7	115	116
3	8	264	-297
3	9	8	0
3	10	66	67
3	11	38	-48
4	0	430	463
4	1	48	41
4	2	6	5
4	3	61	-54
4	4	6	12
4	5	57	52
4	6	54	47
4	7	176	180
4	8	146	-163
4	9	90	-107
4	10	40	-43
5	0	185	-181
5	1	87	93
5	2	8	13
5	3	80	74
5	4	84	83
5	5	97	-97
5	6	58	-43
5	7	36	37
5	8	64	61
5	9	23	-22
6	0	41	41
6	1	58	54
6	2	36	29
6	3	94	-91
6	4	133	-147
6	5	57	51
6	6	34	31
6	7	50	-55
6	8	44	43
7	0	38	-32
7	1	37	30
7	2	187	-194
7	3	168	-189
7	4	104	118
7	5	86	102
8	0	103	-119
8	1	61	-60
8	2	96	-104
8	3	11	-4
8	4	76	76
9	0	37	-28
9	1	84	-102
9	2	105	112
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-1	2	310	-367
-1	3	111	-104
-1	4	473	-514
-1	5	264	271
-1	6	410	426
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-1	8	105	95
-1	9	33	32
-1	10	167	-147
-1	11	119	112
-1	12	11	11
-1	13	76	-70
-1	14	91	-94
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-2	2	57	-47
-2	3	93	-98
-2	4	203	-189
-2	5	155	-159
-2	6	129	-126
-2	7	232	232
-2	8	116	-89
-2	9	43	47
-2	10	66	-58
-2	11	41	-34
-2	12	158	-159
-2	13	51	-42
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-3	3	114	113
-3	4	278	-300
-3	5	218	-203
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-3	8	83	65
-3	9	36	-35
-3	10	37	-27
-3	11	9	-11
-3	12	112	119
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-3	14	111	105
-4	1	139	167
-4	2	196	-213
-4	3	75	-64
-4	4	55	-40
-4	5	41	25
-4	6	5	0
-4	7	165	-174
-4	8	214	203
-4	9	8	-5
-4	10	84	81
-4	11	9	21
-4	12	82	68
-4	13	59	48
-4	14	69	54
-5	1	45	-31
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-5	3	171	158
-5	4	59	47
-5	5	75	-63
-5	6	32	16
-5	7	83	79
-5	8	30	20
-5	9	83	79
-5	10	80	-60
-5	11	123	-125
-5	12	16	2
-5	13	44	-31
-5	14	89	85
-6	1	203	-241
-6	2	183	183
-6	3	274	307
-6	4	5	0
-6	5	36	28
-6	6	13	13
-6	7	61	-55
-6	8	84	-74
-6	9	96	92
-6	10	176	-189
-6	11	93	-66
-6	12	33	42
-6	13	29	-23
-7	1	51	-38
-7	2	162	-147
-7	3	45	-32
-7	4	58	49
-7	5	64	-52
-7	6	76	-71
-7	7	54	37
-7	8	54	42
-7	9	51	27
-7	10	96	85
-7	11	76	79
-7	12	278	-318
-7	13	65	-54
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-8	6	97	103
-8	7	97	-98
-8	8	18	-11
-8	9	38	38
-8	10	37	37
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-9	2	11	2
-9	3	11	-1
-9	4	16	11
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-9	6	107	-113
-9	7	157	-194
-9	8	154	159
-9	9	32	5
-9	10	13	-8
-9	11	27	20
-9	12	154	152
-10	1	11	9
-10	2	44	42
-10	3	13	6
-10	4	13	-11
-10	5	12	-5
-10	6	82	-79
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1	5	109	-107
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1	11	98	-118
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3	2	215	238
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3	8	65	-68
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3	10	6	-14
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4	3	52	45
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4	9	70	-75
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5	3	232	-257
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5	7	70	-89
5	8	136	151
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6	1	40	-30
6	2	123	-130
6	3	32	-31
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6	5	23	-19
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6	7	80	-92
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7	5	11	17
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1	10	12	14
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2	2	104	-98
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2	5	272	-292
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2	10	27	22
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3	9	6	7
3	10	58	-52
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4	1	36	36
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4	5	9	-8
4	6	8	14
4	7	123	130
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5	7	54	50
5	8	23	28
6	0	40	42
6	1	84	85
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6	3	34	-27
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6	5	37	31
6	6	36	32
7	0	12	-3
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7	4	27	-20
7	5	22	-13
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8	1	32	-36
8	2	30	-29
8	3	36	-41
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3	2	66	72
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4	4	8	-7
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Table 1 (*cont.*)

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-6	5	30	-28
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K=	6		
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1	3	132	-131
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1	5	11	5
1	6	11	3
1	7	50	55
1	8	32	35
2	0	54	-52
2	1	160	165
2	2	129	112
2	3	218	-212
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2	5	25	15
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3	2	8	4
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5	2	18	-13
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5	4	40	43
6	0	25	26
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K=	7		
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1	2	11	-10
1	3	11	-12
1	4	11	-4
1	5	62	-61
1	6	76	82
2	0	61	59
2	1	23	20
2	2	70	64
2	3	20	-13
2	4	59	-57
2	5	97	107
3	0	18	23
3	1	11	12
3	2	18	19
3	3	105	129
3	4	105	-28
4	0	23	21
4	1	9	-5
4	2	109	-121
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-3	3	29	-21
-3	4	72	72
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-4	2	12	15
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-4	4	11	9
-4	5	104	-99
-4	6	43	-50
-5	1	32	-38
-5	3	19	-18
-5	2	6	1
-5	4	44	-43
-5	5	37	44

the transform of a projected molecule. This was placed on to the *HnL* sections with its origin coincident with the identified transform origin peaks and rotated until a consistent fit on *H1L*, *H2L*, and *H3L* was obtained. Only the very high transform peaks were used in this procedure and as these were arranged hexagonally, three possible molecular orientations were obtained (for a molecule in which the NO_2 group was coplanar with the ring). These are shown together with the transform fit against *H1L* in Figs. 2(*a*) and 2(*b*).

Molecules in each of these orientations were then packed together on the principle of imino–carbonyl hydrogen bonding across a centre of symmetry. Only fit 3 of Fig. 2(*b*) gave a completely satisfactory packing model and this was used as the basis for an *H0L* structure factor calculation. The agreement index for this was 65%. A single Fourier synthesis on (010) contained no large spurious peaks and showed that the nitro group was approximately coplanar with the pyrimidine ring. The coordinates from this model gave an agreement index of 54% and small movements of the whole molecule reduced this to 45%.

As there were no completely resolved projections, refinement of the structure was carried out with three-dimensional data. Using the x and y parameters from above and the z coordinates calculated on the assumption of a completely planar molecule, a structure factor calculation for seven hundred F_o gave an R value of 46%. A single three-dimensional Fourier synthesis, using a program for the IBM 7070 by McMullan (1962), reduced this to 24% for 1220 observed and unobserved reflections. Differential syntheses, using an IBM 7070 program by Shiono (1962), reduced this further to 14·2%.

Subsequent refinement was carried out with a full matrix least-squares program for the IBM 704 computer written by Busing & Levy (1959). The Hughes (1941) weighting scheme was used and unobserved reflections and ten strong low order F_o suspected of extinction errors were omitted from the calculations. Anisotropic temperature parameters were determined. The second and final least-squares calculation contained hydrogen atoms, in fixed positions deduced from a difference synthesis (see below).

The final R value for 1080 observed reflections was 9·3%; when the 200 unobserved reflections were included at half the minimum observable structure amplitude this was 10%. Results from the final structure factor calculation, scaled up by a factor of 10, are shown in Table 1. The final atomic coordinates and anisotropic thermal parameters are given in Table 2. Mean estimated standard deviations for the positional parameters of C, N, and O atoms are $\sigma(x)=\sigma(y)=\sigma(z)=0{\cdot}0035$ Å. For their thermal parameters the mean standard deviations are $\sigma(B_{jj})=0{\cdot}14$ Å^2 and $\sigma(B_{ij})=0{\cdot}10$ Å^2.

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

Atom	x	y	z
C(2)	0·1222	0·1182	0·1702
C(4)	0·2691	0·3996	0·3016
C(5)	0·2766	0·5156	0·2023
C(6)	0·2050	0·4280	0·0804
N(1)	0·1311	0·2323	0·0749
N(3)	0·1991	0·2052	0·2823
N(5)	0·3619	0·7098	0·2254
O(2)	0·0519	−0·0535	0·1569
O(4)	0·3269	0·4625	0·4144
O(6)	0·2002	0·5142	−0·0133
O(7)	0·4183	0·7823	0·3321
O(8)	0·3821	0·8077	0·1432
H(1)	0·090	0·185	0·005
H(3)	0·208	0·150	0·348
H(6)	0·384	0·593	0·405

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)	1·48	2·14	1·29	−0·04	0·73	−0·25
C(4)	1·48	2·04	0·83	−0·10	0·68	−0·13
C(5)	1·81	1·73	1·38	−0·25	0·86	−0·05
C(6)	1·92	2·06	1·36	0·17	0·82	0·01
N(1)	2·61	1·99	1·01	−0·15	0·80	−0·18
N(3)	2·35	1·99	0·97	−0·43	0·81	−0·23
N(5)	1·74	2·16	1·79	−0·22	0·89	−0·11
O(2)	3·92	2·02	1·17	−0·01	1·14	0·16
O(4)	3·31	2·95	0·74	−0·87	0·79	−0·63
O(6)	2·82	2·08	1·60	−0·81	0·83	−0·26
O(7)	3·53	3·16	1·88	−1·24	0·82	−0·82
O(8)	3·55	3·28	2·38	−1·16	1·31	0·63

The hydrogen atom positions

At the end of the first anisotropic least-squares refinement the lengths of C(2)O(2) and C(6)O(6) showed them to be carbonyl bonds. The nitro group was coplanar with the ring and the bond C(4)O(4) was intermediate in length between a single and a double bond. This would entail contributions from resonance forms possessing C(4)–O(4) and C(4)=O(4) bonds, in which case the position of H(3) (originally supposed to be attached to C5) would be chemically doubtful. There were also five intermolecular distances less than 3 Å, but only two of these were obviously hydrogen bonds. It was therefore important to locate the hydrogen atoms, if the data permitted, for an unambiguous description of the molecular configuration and the intermolecular hydrogen bonding.

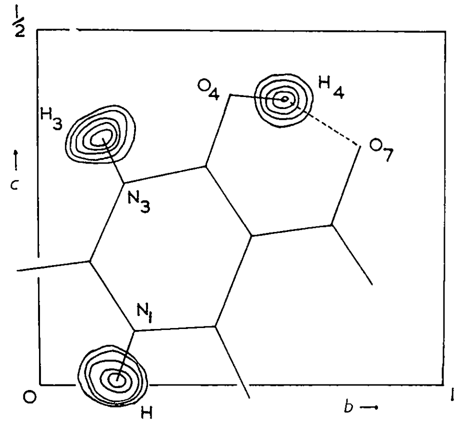


Fig. 3. A composite projection of the hydrogen atom electron density on (100) from $x=0$ to $\frac{1}{2}$. Contours are drawn at 0·2 e.Å^{-2} with the zero contour omitted.

A three-dimensional difference Fourier synthesis, calculated for all reflections with $\sin\theta<0{\cdot}85$, showed the hydrogen atoms as the three largest peaks. After a second least-squares calculation another difference map was computed with the result of a structure factor calculation from which the hydrogen atoms were omitted. The results are shown in Fig. 3. Hydrogen atom electron density peaks are clearly defined against a uniformly low background. The estimated standard deviations of the coordinates derived from those maxima is 0·05 Å as calculated from the formula given by Cruickshank (1949, 1954).

Discussion of the structure

The interatomic distances and valence bond angles are shown in Table 3 and Fig. 4. Their standard deviations are 0·005 Å and 0·3° respectively. Bond angles involving hydrogens have e.s.d.'s of about 3°.

The bond lengths and the hydrogen atom positions show that the molecule is in the 5-nitro-2,6-dioxo-4-hydroxy configuration (III) and not the commonly given trioxo form (I). The molecule is very nearly planar and the best least-squares plane through the non-hydrogen atoms and the atomic deviations from this plane are given in Table 3.

Table 3. *Molecular dimensions and planarity*

Bond	Length	Angles	
C(4)–C(5)	1·408 Å	C(4)–C(5)–C(6)	119·9°
C(6)–C(5)	1·452	C(5)–C(6)–N(1)	113·9
C(4)–N(3)	1·348	C(6)–N(1)–C(2)	126·9
C(6)–N(1)	1·382	N(1)–C(2)–N(3)	115·8
N(1)–C(2)	1·366	C(2)–N(3)–C(4)	124·0
N(3)–C(2)	1·361	N(3)–C(4)–C(5)	119·3
N(5)–C(5)	1·406	N(3)–C(4)–O(4)	115·3
C(2)–O(2)	1·225	N(1)–C(6)–O(6)	119·8
C(4)–O(4)	1·302	N(1)–C(2)–O(2)	122·7
C(6)–O(6)	1·223	N(3)–C(2)–O(2)	121·5
N(5)–O(7)	1·259	C(5)–C(4)–O(4)	125·5
N(5)–O(8)	1·222	C(5)–C(6)–O(6)	126·3
		C(5)–N(5)–O(7)	119·4
N(1)–H(1)	0·83	C(5)–N(5)–O(8)	120·7
N(3)–H(3)	0·83	O(7)–N(5)–O(8)	120·0
		C(6)–C(5)–N(5)	121·6
O(4)–H(4)	0·99	C(4)–C(5)–N(5)	118·4
		C(4)–O(4)–H(4)	99·0

Equation to the plane:

$$0{\cdot}8758x-0{\cdot}4681y-0{\cdot}2206z-0{\cdot}1518=0$$

Deviations from plane

C(2)	0·012 Å	N(3)	0·065 Å	O(7)	−0·041 Å
C(4)	−0·007	N(5)	0·010	O(8)	0·096
C(5)	−0·028	O(2)	0·000	H(1)	0·006
C(6)	−0·012	O(4)	−0·035	H(3)	0·105
N(1)	−0·003	O(6)	−0·057	H(4)	0·044

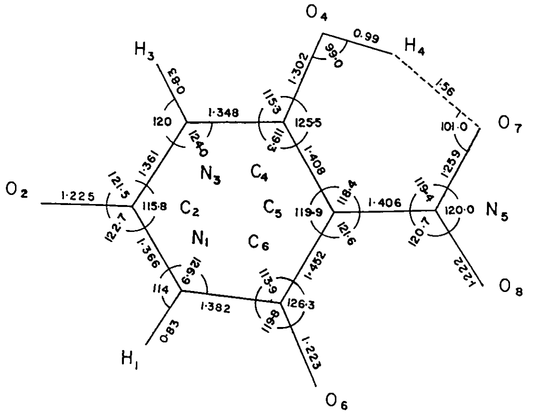
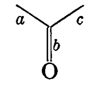


Fig. 4. Dimensions of the molecule in anhydrous dilituric acid.

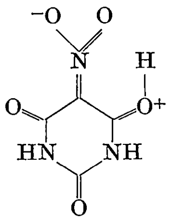
Bond orders calculated from Pauling's (1960) data show that generally the bonds are of intermediate character. In particular the formal hydroxyl bond C(4)O(4) of 1·302 Å is only 43% double bond and is significantly shorter than the longer bond in carboxylic acids and esters, 1·36 Å (Sutton, 1958). It is interesting that the dimensions of the 'urea' half of the molecule –NH.CO.NH– are not significantly different from those of the same parts of the molecules of barbituric acid (1) (Jeffrey *et al.*, 1961; Bolton, 1963), uracil (2) (Parry, 1954) and thymine (3) (Gerdil, 1961), although the formal valence-bond structures of the rest of the pyrimidine ring are not the same in the four molecules:

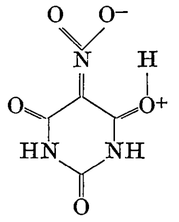


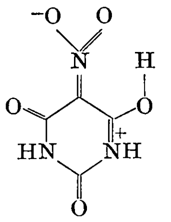
	(1)	(2)	(3)
a	1·363	1·34	1·361
b	1·223	1·23	1·234
c	1·364	1·38	1·355

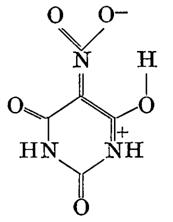
The C(5)N(5) bond length of 1·406 Å is possibly the shortest reliable observed C–NO_2 distance to date. It is significantly shorter than the average of 1·48 Å, found by Trotter (1960) for five nitro-aromatic hydrocarbons and the more accurate values of 1·454 ± 0·006, 1·442 ± 0·006, 1·442 ± 0·006, and 1·445 ± 0·003 Å for 4-nitroaniline (Trueblood, Goldish & Donohue, 1961) and α and β 4-nitrophenol (Coppens, 1960). This shortening, together with the coplanarity of the nitro group and the pyrimidine ring, suggests appreciably more resonance interaction across the C–N bond than in those compounds.

The difference between the C–N bond lengths in nitro and amino derivatives of benzene can be qualitatively explained by assuming that only valence bond diagrams with the maximum number of double bonds are important (*e.g.* Sakurai, Sundralingam & Jeffrey, 1962). Seven such structures can be written for the dilituric acid molecule and four of these (IV, V, VI and VII) contain C(5)=N(5) double bonds. If these make appreciable contributions to the ground state of the molecule, the observed shortening of C(6)N(1) and C(6)O(6) from formal single-bond values as well as the short C–NO_2 bond are qualitatively accounted for.

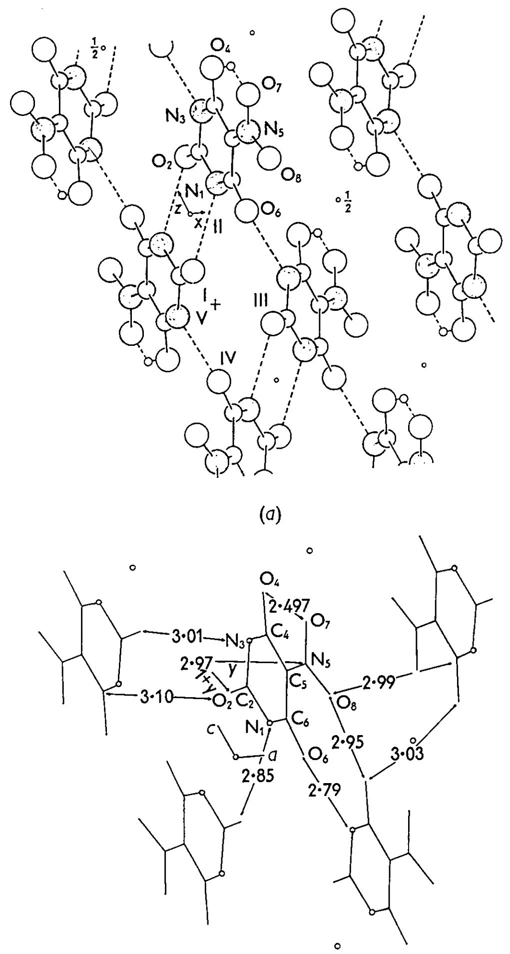

(IV)


(V)


(VI)


(VII)

The intramolecular hydrogen bond (O(4)H(4)O(7), Fig. 4) is 2·497 Å compared with 2·57, 2·59 and 2·44 in nitroguanidine (Bryden, Burkardt, Hughes & Donohue, 1956), salicylic acid (Cochran, 1953), and potassium hydrogen maleate (Darlow & Cochran, 1961) respectively. The hydrogen atom is closer to the line of centres of the oxygen atoms than in the longer hydrogen bond in salicylic acid but not as close as in the very short hydrogen bond in the maleate ion. There appears to be a qualitative correlation between colinearity of the O–H · · · O bond and its length.



(*a*)

(*b*)

Fig. 5. The (010) projection of the structure of anhydrous dilituric acid. (*a*) The hydrogen bonding scheme. Dotted lines indicate hydrogen bonds. Molecules I, II, III, IV and V (at x, $1+y$, z) make up one complete turn of a spiral of hydrogen bonded molecules. (*b*) Closest intermolecular approaches in the structure of anhydrous dilituric acid.

Fig. 5(*a*) shows the projection of the structure on (010). The molecules are hydrogen bonded into interlocking spirals with axes perpendicular to b; (I), (II), (III), (IV) and (V) (at x, $1+y$, z) represent one turn of a spiral. All the oxygen and nitrogen atoms (except O8 of the nitro group) and all available hydrogens take part in the hydrogen bonding system. The parabanic acid (Davies & Blum, 1955) and anhydrous barbituric acid (Bolton, 1963) structures, which have the same number of oxygen and nitrogen atoms and available protons for hydrogen bonding, are made up of puckered sheets and ribbons of molecules respectively. The number of molecules in a hydrogen bonded group is n^2 and $2n$ in these and $2n^2$ in dilituric acid; therefore in this sense the last structure is the more compactly hydrogen bonded. This corresponds to the unusually high density of the

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

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

	Distances (Å)		Distances (Å)
C(2)(IV)–C(4)(XII)	3·89	N(1)(II)–O(6)(VI)	3·19
C(2)(I)–C(5)(XII)	3·99	N(1)(III)–O(4)(VII)	3·27
C(2)(II)–N(1)(I)	3·67	N(1)(IV)–O(7)(VIII)	3·77
C(2)(I)–N(5)(XII)	3·24	N(1)(I)–O(8)(XII)	3·38
C(2)(II)–O(6)(VI)	3·61	N(3)(I)–N(5)(XII)	3·60
C(2)(III)–O(6)(I)	3·65	N(3)(IV)–O(2)(I)	3·01
C(2)(IV)–O(4)(XII)	3·88	N(3)(I)–O(7)(XII)	3·21
C(2)(II)–O(2)(I)	3·62	N(3)(I)–O(8)(XII)	3·69
C(2)(IV)–O(2)(I)	3·64	N(3)(IV)–O(8)(VIII)	3·57
C(2)(I)–O(7)(XII)	3·36	N(5)(IV)–N(5)(V)	3·89
C(2)(I)–O(8)(XII)	3·14	N(5)(I)–O(2)(VI)	2·97
C(4)(III)–N(1)(I)	3·97	N(5)(IV)–O(7)(VIII)	3·54
C(4)(IV)–N(5)(VIII)	3·63	N(5)(IV)–O(8)(VIII)	3·36
C(4)(III)–O(6)(I)	3·60	O(6)(II)–O(6)(VI)	3·71
C(4)(IV)–O(2)(I)	3·10	O(6)(III)–O(4)(VII)	3·42
C(4)(IV)–O(7)(VIII)	3·77	O(6)(III)–O(4)(IX)	3·67
C(4)(IV)–O(8)(VIII)	2·99	O(6)(I)–O(2)(VI)	3·90
C(5)(IV)–N(5)(VIII)	3·57	O(6)(II)–O(2)(I)	3·66
C(5)(I)–O(2)(VI)	3·29	O(6)(III)–O(2)(VII)	3·64
C(5)(IV)–O(2)(I)	3·91	O(6)(III)–O(7)(IX)	3·39
C(5)(IV)–O(7)(VIII)	3·25	O(6)(IV)–O(7)(VIII)	3·58
C(5)(IV)–O(8)(VIII)	3·19	O(4)(II)–O(4)(X)	3·03
C(6)(II)–C(6)(VI)	3·55	O(4)(IV)–O(2)(I)	3·17
C(6)(II)–N(1)(VI)	3·57	O(4)(II)–O(7)(X)	3·38
C(6)(III)–N(3)(VII)	3·62	O(4)(III)–O(8)(VI)	2·95
C(6)(II)–O(6)(VI)	3·42	O(4)(IV)–O(8)(VIII)	3·08
C(6)(III)–O(4)(VII)	3·56	O(2)(II)–O(2)(I)	3·55
C(6)(I)–O(2)(VI)	3·77	O(2)(I)–O(7)(XII)	3·31
C(6)(II)–O(2)(I)	3·72	O(2)(I)–O(8)(XII)	3·14
C(6)(IV)–O(7)(VIII)	3·26	O(7)(III)–O(8)(VI)	3·87
N(1)(II)–N(1)(I)	3·74	O(7)(IV)–O(8)(V)	3·70
N(1)(III)–N(3)(VII)	3·77	O(7)(IV)–O(8)(VIII)	3·42
N(1)(I)–N(5)(XII)	3·92		
N(1)(II)–O(2)(I)	2·85*	O(4)(I)–O(7)(I)	2·50*
H(1)(II)–O(2)(I)	2·05	H(4)(I)–O(7)(I)	1·57
N(3)(III)–O(6)(I)	2·79*		
H(3)(III)–O(6)(I)	1·97		

* Hydrogen-bond distances.

crystals of 1·874 g.cm^{-3}, compared with 1·721 and 1·560 for parabanic and barbituric acids.

Apart from the hydrogen bonds N(1)O(2) and N(3)O(6), of 2·85 and 2·79 Å there are three intermolecular approaches less than 3 Å (Table 4 and Fig. 5(*b*)). The N(5)O(2) and O(8)O(4) distances of 2·97 Å and 2·95 Å correspond to normal van der Waals contacts. The distance of 2·99 Å between the non-hydrogen-bonded oxygen atom O(8) and the carbonyl carbon atom C(4) is about 0·10 Å less than the sum of the van der Waals radii given by Pauling (1960). The direction of this non-bonding interaction is similar to those observed in anhydrous barbituric acid (Bolton, 1963) and the other examples quoted in the introduction to this paper.

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