p–p. Les angles que forment les liaisons hydrogène avec les directions de valence S–O des ions $S_2O_6^{--}$, sont proches de 110°. L'hybridation des oxygènes semble donc être uniformément sp^3.

Malgré la proximité relative, des protons appartenant à différentes molécules d'eau, les raies de résonance ne font pas apparaître de structure autre qu'un élargissement symétrique. L'approximation faite en considérant des molécules d'eau isolées, est donc justifiée par l'interprétation des résultats.

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The Crystal and Molecular Structure of 1,3,7,9-Tetramethyluric Acid.

By D. June Sutor

Birkbeck College Crystallography Laboratory, 21, Torrington Square, London, W.C. 1, England

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Two polymorphic forms of 1,3,7,9-tetramethyluric acid have been found. The form crystallizing as needles is monoclinic, space group $P2_1/a$ with four molecules in a unit cell of dimensions

$$a = 10{\cdot}11,\ b = 14{\cdot}89,\ c = 6{\cdot}75\ \text{Å};\ \beta = 100{\cdot}4°.$$

Atomic parameters determined from the *hk*0 and 0*kl* sharpened Patterson functions and from structure-factor graphs were refined, together with anisotropic temperature factors, by a three-dimensional least-squares process. The standard deviation in bond length is 0·011 Å. Bond lengths in the five-membered ring are significantly different from those in a purine where this ring does not contain methyl groups or an oxygen atom as substituents. Molecules are stacked almost perpendicular to the *c* axis, in parallel planes of alternate spacing 3·39, 3·36 Å, and these blocks of molecules are related by screw axes. Short intermolecular methyl–oxygen distances indicate that C–H · · · O hydrogen bonds probably arising from activation of the C–H group are present in the crystal structure.

Introduction

The determination of the crystal structure of 1,3,7,9-tetramethyluric acid forms part of a programme of work on the structures of pyrimidines, purines and related compounds. Theophylline and caffeine, di- and trimethyl substituted hydroxy purines respectively have been the subjects of previous work (Sutor, 1958*a*, *b*). The structure of a tetramethyl purine derivative in which the base is fully substituted (see Fig. 1) is now given. Unlike the other two, it contains no water of crystallization, and crystallographically it is not isomorphous with them. A preliminary account of this work has been published (Sutor, 1960).

Experimental

Tetramethyluric acid ($C_9H_{12}N_4O_3$) used in this investigation was kindly supplied by Prof. E. Boyland of the Chester Beatty Research Institute. Crystals were obtained by allowing a hot aqueous solution of the substance to cool slowly. Two polymorphic forms separated from different recrystallizations, but conditions favouring the formation of one in preference to the other are not known.

The form which is obtained more readily is that described by Groth when his *c* axis is halved, and a preliminary account of its crystal structure has been published by de Santis, Giglio & Liquori (1960), who give the cell dimensions as:

$$a = 15{\cdot}59,\ b = 8{\cdot}87,\ c = 8{\cdot}46\ \text{Å};$$
$$\beta = 118°,\ V = 1033\ \text{Å}^3.$$

Like crystals of theophylline, these can be referred to the space group $P2_1/a$ if weak 'forbidden' reflexions of the type *h*0*l* with *h* odd are ignored. My work has shown that the number of 'forbidden' ones is about 17%.

Crystals of the other form which is now to be described in detail are needles elongated along the c axis, and twinning is quite frequent. The unit-cell dimensions obtained from rotation and Weissenberg photographs are:

$$a=10\cdot11,\ b=14\cdot89,\ c=6\cdot75\ \text{Å};$$
$$\beta=100\cdot4^\circ,\ V=999\ \text{Å}^3.$$

The density determined from a mixture of carbon tetrachloride and acetone is 1·482 g.cm.$^{-3}$, and that calculated for a unit cell containing four molecules 1·488 g.cm^{-3}. The space group is $P2_1/a\text{–}C_{2h}^5$, there being no 'forbidden' reflexions observable on any of the photographs. This, together with the smaller volume of the unit cell and short c axis suggested these crystals were more suitable for a full structure determination. Consequently no further work on the other form was undertaken.

For intensity measurements, the $hk0$, $hk1$, $hk2$ and $hk3$ reflexions were recorded with Cu $K\alpha$ radiation on Weissenberg photographs, taken about the c axis, using the multiple-film technique and the equi-inclination method. The shape of the crystals, and the difficulty in cutting them, prevented reliable data being obtained about other axes. Accordingly only the $0kl$ reflexions were collected for the determination of approximate z co-ordinates. Visual estimations of the intensities of the 973 observed reflexions (excluding the $0kl$'s) were made, and the resulting values converted to structure amplitudes in the usual way. Correction curves for the variation in reflexion spot-shape on the $hk1$, $hk2$ and $hk3$ layer lines were derived from the harmonic mean of equivalent reflexions for which extended and contracted values could be measured (Phillips, 1954). Six of the $hk3$ low-angle reflexions which were well outside the experimentally determined curve were later corrected by scaling to the calculated structure factors.

Determination and refinement of the atomic co-ordinates

As the c axis is fairly short, the molecules are likely to lie in planes almost perpendicular to it. Except for a keto- and two methyl groups of the five-membered ring, tetramethyluric acid consists of a hexa-substituted six-membered ring assumed to be planar. The sharpened $hk0$ Patterson function shows, around the origin, characteristic and easily recognizable peaks corresponding to the equal and parallel vectors within this symmetrical group. The function also contains a large peak which represents equivalent vectors between two of the symmetrical groups related by a centre of symmetry of the space group and which is located at a distance from the origin equal to the vector distance between the molecular centres of these groups. There was no ambiguity in fixing the orientation of the group, as one side of the ring is parallel to the a axis. Because of the special orientation of the rings in this projection, there are peaks corresponding to intermolecular vectors between groups related by the glide plane. Two possible positions which also satisfied packing conditions were indicated for the ring. Structure factor graphs for the reflexions 200, 400, 020, 040, 110, 120 and 210 were used to select one position which also corresponded to a better vector distribution, and to locate the remaining four atoms. Nevertheless, the same orientation of the whole molecule in the other position—the only other arrangement giving reasonable agreement between observed and calculated structure factors—was not discarded until refinement proved impossible. The z co-ordinates of the atoms were determined from the $0kl$ sharpened Patterson function and from a consideration of the possible molecular packing. For the usual separation between molecular planes, these co-ordinates must be close to a quarter.

Two-dimensional refinement

The atomic co-ordinates were refined by two dimensional Fourier and difference syntheses (Cochran, 1951), and finally by the method of least-squares. All calculations were carried out on the Ferranti Mercury computer. In the least-squares refinement, use was made of Dr Rollett's structure factors-least-squares programme with scattering factors of Berghuis *et al.* (1955) for carbon, nitrogen and oxygen atoms, and that of McWeeny (1951) for the hydrogen atoms. The programme evaluates the block-diagonal approximation—3×3 and 6×6 matrices for the co-ordinates and temperature factors of each atom and a 2×2 matrix for the scale factor and overall B-value. Two reflexions 110 and 200 which suffer from extinction, and all non-observed ones were given zero weight; all other reflexions were assigned equal weights. When the R-factor for the $hk0$ terms had reached 16%, the difference synthesis indicated the positions of all twelve hydrogen atoms which were included in subsequent calculations. However, it proved impossible to determine their z co-ordinates with any certainty. In both projections, the overall isotropic temperature factor was 3·3 Å^2. The R-factors at the end of the two-dimensional refinement were 11·2% for the (001) projection and 19·0% for the (100). These values exclude reflexions too small to be observed, and 110 and 200. The (001) projection calculated from the final co-ordinates from the three dimensional refinement is shown in Fig. 1.

Three-dimensional refinement

It was desirable to continue the least-squares refinement in three dimensions because of the poor $0kl$ data, and because a short intermolecular distance of 2·96 Å between a methyl group and oxygen atom needed

Table 1. *Observed and calculated structure factors for* $F_{000}=236$ (*two molecules only*)

All values have been multiplied by ten. '*a*' indicates off film

k	$\|F_o\|$	F_c
	0k0	
2	397	515
4	132	-134
6	123	-123
8	35	34
10	116	110
12	175	-168
14	99	-99
16	<13	0
18	17	14
	1k0	
1	380	486
2	163	-175
3	168	-169
4	31	31
5	106	95
6	38	-18
7	54	-50
8	58	45
9	74	57
10	45	34
11	84	-80
12	53	-53
13	126	-114
14	11	-2
15	<12	1
16	31	31
17	20	16
18	<8	3
19	21	22
	2k0	
0	222	-235
1	60	-65
2	177	-196
3	92	78
4	12	-6
5	65	64
6	97	-82
7	45	24
8	<10	5
9	81	80
10	22	-16
11	<12	11
12	64	-56
13	40	-35
14	<12	-2
15	<12	-6
16	<12	1
17	12	4
18	32	25
19	6	-10
	3k0	
1	15	-22
2	21	-22
3	132	129
4	32	28
5	194	-164
6	171	173
7	61	-59
8	73	62
9	<11	8
10	86	-81
11	<10	9
12	50	-43
13	40	34
14	15	-14
15	14	-15
16	14	10
17	<9	-10
18	<7	-3
	4k0	
0	299	-311
1	79	80
2	38	32
3	47	-43
4	115	115
5	34	28
6	65	55
7	90	87
8	<11	-15
9	91	-79
10	75	-67
11	19	-15
12	67	62
13	44	33
14	21	24
15	<11	-1
16	<10	6
17	<8	0
18	<6	-10
	5k0	
1	46	32
2	118	103
3	10	-6
4	29	-31
5	16	-11
6	14	-12
7	93	96
8	<12	4
9	14	-12
10	101	88
11	35	26
12	120	106
13	<10	5
	5k0	
14	<11	8
15	29	-12
16	18	-17
17	19	17
	6k0	
0	142	134
1	34	31
2	33	26
3	25	18
4	115	-105
5	68	-66
6	10	2
7	121	-104
8	68	58
9	19	20
10	15	8
11	85	73
12	<10	1
13	<10	8
14	57	-44
15	<9	7
16	12	7
	7k0	
1	73	-61
2	72	65
3	52	-38
4	14	-16
5	55	-48
6	213	-205
7	<12	7
8	161	-150
9	<13	0
10	<13	8
11	23	-16
12	<10	-7
13	15	-9
14	<9	-9
15	11	7
	8k0	
0	32	32
1	11	4
2	23	16
3	<13	-12
4	70	-60
5	111	-92
6	91	-80
7	104	-100
8	<12	17
9	<12	-6
10	22	25
11	<12	11
12	<10	-6
13	<9	-9
14	<8	4
	9k0	
1	84	79
2	56	-47
3	25	23
4	49	-40
5	28	-17
6	13	5
7	13	-23
8	34	23
9	25	23
10	<10	-13
11	<10	-4
12	<10	0
13	18	-14
	10k0	
0	<13	20
1	<12	-8
2	17	-15
3	11	-1
4	21	23
5	14	6
6	34	28
7	16	14
8	<10	-7
9	14	-11
10	<8	-4
11	15	-14
12	20	-27
	11k0	
1	<11	13
2	<11	-11
3	35	-29
4	16	13
5	12	9
6	<9	7
7	9	-6
8	11	15
9	<6	-2
	12k0	
0	28	20
1	<9	-6
2	15	11
3	10	9
4	30	20
5	<7	-4
6	11	9
	0k1	
0	a	95
1	a	-56
2	6	-2
3	61	59
4	50	-57
5	39	-44
6	80	-91
7	245	-239
8	<8	-2
9	49	-44
10	40	51
11	81	-81
12	16	20
13	97	-109
14	<10	9
15	16	-23
16	<9	-10
17	16	-18
18	<7	-1
19	5	-8
	1k1	
1	22	34
2	73	-70
3	45	49
4	106	108
5	<6	-17
6	178	177
7	120	-120
8	62	58
9	82	87
10	23	-30
11	20	25
12	62	-65
13	25	31
14	<10	8
15	<10	9
16	<9	14
17	33	-33
18	8	-9
19	6	13
	2k1	
0	56	-62
1	33	-30
2	113	-126
3	98	-108
4	268	273
5	117	120
6	62	88
7	252	247
8	<8	-4
9	38	38
10	19	15
11	10	20
12	58	-70
13	47	52
14	<10	12
15	14	15
16	32	-30
17	10	-7
18	8	-9
	3k1	
1	153	156
2	73	-78
3	260	-260
4	58	-73
5	25	-22
6	172	174
7	31	-44
8	87	74
9	76	85
10	43	-48
11	11	-9
12	18	19
13	65	-72
14	11	18
15	11	-12
16	<9	-4
17	11	-13
18	<5	-4
	4k1	
0	334	366
1	45	-35
2	<7	3
3	<7	-13
4	43	-49
5	92	79
6	38	35
7	78	69
8	16	-26
9	33	-28
10	<10	12
11	46	-57
12	49	-53
13	11	-9
14	21	-23
15	<9	13
16	7	6
17	<6	9
	5k1	
1	191	183
2	8	8
3	140	129
4	24	26
	5k1	
5	91	91
6	68	-74
7	10	21
8	26	-20
9	42	-47
10	33	44
11	43	-45
12	<10	-2
13	20	-91
14	12	-13
15	<8	-5
16	<7	-2
17	<5	4
	6k1	
0	15	12
1	26	-27
2	75	86
3	29	-30
4	38	-45
5	23	-17
6	74	-83
7	<10	-2
8	18	21
9	47	48
10	9	-12
11	24	26
12	<10	9
13	15	-15
14	<8	-12
15	<7	-3
16	<5	2
	7k1	
1	98	-106
2	34	33
3	<10	17
4	44	42
5	79	-85
6	99	107
7	<10	-5
8	45	45
9	14	-20
10	<10	-2
11	12	-9
12	<9	6
13	16	18
14	<7	10
15	<5	0
	8k1	
0	24	-14
1	45	47
2	18	19
3	28	29
4	29	-28
5	45	50
6	23	-19
7	44	54
8	<10	12
9	20	-22
10	20	-25
11	<9	0
12	<8	-5
13	<9	2
14	16	-17
	9k1	
1	89	95
2	31	-34
3	18	-25
4	31	-36
5	46	-52
6	14	20
7	10	7
8	<9	-7
9	15	18
10	19	-22
11	10	11
12	20	-21
13	14	-16
	10k1	
0	33	41
1	10	-11
2	<10	1
3	<10	-6
4	<9	-4
5	<9	1
6	27	20
7	16	-15
8	22	15
9	<7	-1
10	8	8
11	6	-5
	11k1	
1	<8	-1
2	<8	-3
3	<8	-2
4	<8	3
5	13	14
6	39	-32
7	10	10
8	12	-12
9	6	11
	12k1	
0	<6	-1
1	15	-16
2	<6	-7
3	19	-19
4	10	-10
5	22	-26
	1k$\bar{1}$	
1	141	-127
2	41	46
3	20	12
4	89	-83
5	149	184
6	46	40
7	123	123
8	40	37
9	91	-92
10	31	30
11	29	-41
12	103	111
13	31	-34
14	31	35
15	<10	-7
16	10	5
17	22	21
18	<7	5
19	7	-12
	2k$\bar{1}$	
0	82	86
1	56	54
2	59	53
3	9	25
4	290	-291
5	169	-171
6	7	-8
7	237	-230
8	18	19
9	46	-42
10	26	-23
11	31	33
12	23	20
13	18	-23
14	27	-33
15	16	-22
16	31	32
17	<8	0
18	9	11
19	3	10
	3k$\bar{1}$	
1	5	14
2	90	84
3	85	92
4	49	49
5	157	-162
6	192	-191
7	30	24
8	130	-116
9	41	-39
10	23	24
11	19	31
12	42	-48
13	49	56
14	29	-33
15	16	12
16	<9	12
17	25	25
18	<6	3
	4k$\bar{1}$	
0	400	-385
1	88	105
2	97	102
3	64	67
4	153	148
5	98	-89
6	8	17
7	146	-143
8	<9	11
9	24	28
10	45	-58
11	53	66
12	53	53
13	<10	-8
14	35	35
15	<9	-12
16	<8	3
17	<7	-8
18	<6	4
	5k$\bar{1}$	
1	216	-212
2	31	33
3	58	-56
4	68	-62
5	106	-109
6	9	3
7	9	-9
8	21	9
9	40	43
10	14	13
11	46	45
12	13	20
13	38	41
14	<10	-3
15	<9	-2
16	<7	-11
	5k$\bar{1}$	
17	<6	1
	6k$\bar{1}$	
0	140	-137
1	22	17
2	143	-147
3	11	11
4	45	-32
5	58	58
6	19	17
7	58	63
8	10	-19
9	42	-43
10	26	30
11	42	-41
12	18	25
13	16	17
14	9	19
15	11	11
16	<6	0
	7k$\bar{1}$	
1	51	50
2	<9	4
3	<9	-19
4	10	14
5	114	119
6	59	-67
7	13	16
8	53	-46
9	<10	-3
10	20	-23
11	<10	0
12	<10	-1
13	14	-16
14	<8	2
15	<7	4
	8k$\bar{1}$	
0	101	118
1	55	-67
2	11	13
3	51	-43
4	21	15
5	79	-81
6	28	29
7	80	-84
8	<10	4
9	13	15
10	34	40
11	<9	-8
12	<9	-6
13	8	-9
14	<8	4
15	8	-10
	9k$\bar{1}$	
1	66	-72
2	<10	5
3	11	11
4	21	25
5	45	52
6	41	-49
7	<10	-6
8	<10	4
9	<9	-1
10	22	21
11	<8	-1
12	10	11
13	17	18
14	7	11
	10k$\bar{1}$	
0	78	-85
1	26	28
2	18	-22
3	37	42
4	29	34
5	<10	-2
6	<10	4
7	<9	-4
8	20	-15
9	15	14
10	15	-15
11	23	21
12	6	1
	11k$\bar{1}$	
1	<9	-1
2	<9	1
3	<9	1
4	19	-16
5	23	-21
6	26	23
7	25	-23
8	15	13
9	14	-12
	12k$\bar{1}$	
0	47	-1
1	14	16
2	<7	3
3	10	11
4	<7	5
5	31	28
6	<6	9
7	27	29
	13k$\bar{1}$	
1	5	8
2	5	10
	0k2	
0	a	-1229
1	32	34
2	259	-257
3	28	5
4	82	85
5	5	3
6	38	36
7	7	1
8	7	-15
9	18	-21
10	58	-61
11	<8	8
12	135	138
13	21	26
14	73	79
15	<8	-10
16	<8	-5
17	8	-11
18	14	-17
	1k2	
1	69	83
2	74	67
3	134	113
4	65	-66
5	53	-58
6	10	25
7	33	32
8	45	-47
9	14	-8
10	54	-61
11	54	58
12	26	31
13	57	60
14	14	17
15	<7	-2
16	10	-14
17	14	-16
18	<4	3
	2k2	
0	140	114
1	35	48
2	8	-1
3	50	-46
4	56	61
5	97	-101
6	149	143
7	72	-71
8	10	-15
9	27	-31
10	<8	-12
11	33	26
12	8	3
13	26	26
14	<8	4
15	<7	7
16	8	16
17	<5	-2
18	15	-16
	3k2	
1	81	87
2	40	38
3	134	-131
4	<5	0
5	42	44
6	136	-135
7	<7	-8
8	25	-25
9	23	24
10	94	105
11	8	-1
12	21	24
13	38	-43
14	8	-7
15	<7	2
16	6	-9
17	<5	5
	4k2	
0	148	145
1	76	-76
2	21	-17
3	6	0
4	45	-52
5	15	24
6	57	-68
7	21	-26
8	18	-16
9	12	5
10	44	54
11	54	-55
12	35	-44
13	48	-53
14	<7	-9
15	<7	11
16	5	-15
17	<5	7
	5k2	
1	97	-103
2	69	-61
	5k2	
3	28	31
4	21	22
5	49	56
6	53	60
7	56	-67
8	8	-3
9	12	-6
10	90	-92
11	19	-22
12	73	-76
13	12	15
14	<7	-5
15	23	22
16	6	9
	6k2	
0	<7	4
1	28	-29
2	16	17
3	30	-42
4	40	43
5	80	91
6	8	-5
7	162	163
8	16	-13
9	29	27
10	13	20
11	24	-27
12	7	5
13	8	8
14	19	22
15	<5	-5
	7k2	
1	29	35
2	37	-43
3	18	20
4	21	23
5	46	52
6	165	164
7	24	22
8	106	109
9	<8	-4
10	<7	-10
11	<7	6
12	<7	4
13	<6	0
14	8	13
	8k2	
0	84	-89
1	19	17
2	37	-47
3	33	38
4	26	28
5	39	39
6	52	62
7	17	19
8	<8	-10
9	16	-7
10	21	-27
11	6	-3
12	10	10
13	<4	-2
	9k2	
1	30	-40
2	18	21
3	10	-12
4	10	15
5	16	-21
6	16	-16
7	<7	6
8	13	-12
9	10	-9
10	17	19
11	14	17
	10k2	
0	<7	-18
1	<7	2
2	21	6
3	8	-5
4	<7	1
5	9	-6
6	15	-16
7	8	-11
8	<5	8
9	<4	2
	11k2	
1	17	-19
2	8	8
3	<5	8
4	5	-9
5	8	-10
6	<4	0
	1k$\bar{2}$	
1	a	-925
2	255	227
3	64	60
4	16	8
5	26	42
6	7	4
7	49	52
	1k$\bar{2}$	
8	41	-41
9	87	-87
10	<7	9
11	51	50
12	34	47
13	139	139
14	8	-12
15	16	17
16	15	-25
17	8	-8
18	<5	-4
	2k$\bar{2}$	
0	4	4
1	154	145
2	122	118
3	20	-24
4	<5	-19
5	24	-15
6	<6	-10
7	<6	-7
8	9	-11
9	73	-73
10	16	27
11	14	8
12	94	96
13	19	24
14	13	11
15	10	-13
16	13	-15
17	10	-13
18	17	-22
	3k$\bar{2}$	
1	94	96
2	31	-39
3	15	-16
4	60	-76
5	132	131
6	63	-67
7	59	54
8	74	-68
9	<7	-16
10	<8	7
11	24	22
12	26	26
13	<8	-3
14	16	23
15	<8	4
16	<7	-4
17	<6	0
18	<4	0
	4k$\bar{2}$	
0	168	174
1	41	-41
2	52	-68
3	36	51
4	55	-61
5	50	-47
6	33	40
7	122	-115
8	22	36
9	67	76
10	39	33
11	52	57
12	40	-52
13	<8	5
14	15	-21
15	<7	0
16	<6	9
17	6	-8
	5k$\bar{2}$	
1	83	84
2	94	-93
3	46	-47
4	32	40
5	61	-68
6	31	-45
7	52	-63
8	19	19
9	40	47
10	8	-21
11	21	-20
12	76	-79
13	25	-31
14	7	-9
15	<7	-1
16	<6	11
17	7	-11
	6k$\bar{2}$	
0	139	-136
1	46	-63
2	27	-30
3	8	0
4	84	100
5	25	18
6	-17	-18
7	31	32
8	53	-65
9	57	-42
10	24	-24
11	105	-108
12	<8	-11
13	83	-87
14	43	41
15	<6	-1
16	<5	-5

Table 1 (*cont.*)

k	$\|F_o\|$	F_c
	$7k\bar{2}$	
1	14	-11
2	30	-34
3	42	43
4	10	24
5	58	·61
6	134	133
7	31	-36
8	116	114
9	21	-20
10	15	-23
11	8	6
12	<8	-1
13	27	23
14	<6	1
15	<5	8
	$8k\bar{2}$	
0	40	45
1	25	-31
2	19	22
3	17	-18
4	59	67
5	114	108
6	52	53
7	161	160
8	16	-27
9	35	37
10	<8	-7
11	<7	-10
12	11	11
13	8	14
14	<5	-4
	$9k\bar{2}$	
1	65	-67
2	30	38
3	<8	-1
4	56	58
5	63	69
6	41	42
7	13	26
8	10	-6
9	25	-34
10	<7	-5
11	<6	-7
12	<5	3
13	<4	6
	$10k\bar{2}$	
0	40	-43
1	14	19
2	18	-21
3	17′	23
4	17	-25
5	<8	5
6	12	-13
7	22	-19
8	<7	6
9	<6	6
10	<5	-1
11	17	18
12	10	18
	$11k\bar{2}$	
1	<7	3
2	<7	6
3	18	22
4	16	-16
5	19	-25
6	<6	-5
7	<6	-3
8	<5	-9
	$12k\bar{2}$	
0	27	-33
1	10	15
2	<6	-3
3	<5	-3
4	<5	0
5	<5	-7
	$0k3$	
0	73	-71
1	48	51
2	35	-34
3	21	-26
4	35	42
5	56	-60
6	97	106
7	37	49
8	8	-3
9	33	31
10	63	-73
11	66	62
12	26	-31
13	60	62
14	14	-18
15	<9	-7
16	14	16
17	9	9
	$1k3$	
1	55	64
2	89	86
3	69	-69
4	17	-26
5	73	-84
6	218	-194
7	17	26
8	100	-102
9	40	-40
10	<9	-5
11	14	19
12	9	-2
13	8	-2
14	20	-25
15	<8	-9
16	8	-14
17	29	29
	$2k3$	
0	61	-65
1	11	7
2	59	72
3	52	64
4	7	-8
5	44	-31
6	20	-20
7	137	-141
8	26	-21
9	17	-11
10	34	-36
11	20	-24
12	65	70
13	32	-38
14	18	14
15	<8	-1
16	20	18
17	<4	7
	$3k3$	
1	163	-161
2	26	20
3	144	155
4	7	4
5	32	40
6	93	-94
7	18	25
8	40	-36
9	38	-50
10	44	54
11	9	6
12	12	10
13	48	56
14	<7	-6
15	<6	5
16	<5	-8
	$4k3$	
0	228	-188
1	14	9
2	67	-64
3	22	-31
4	58	-61
5	27	-18
6	54	-63
7	<9	3
8	31	31
9	<10	-4
10	32	28
11	10	15
12	39	40
13	8	12
14	14	15
15	<6	-1
16	<4	-7
	$5k3$	
1	105	-102
2	8	16
3	71	-74
4	<9	-2
5	7	10
6	47	56
7	12	6
8	<10	-2
9	17	17
10	44	-45
11	14	15
12	<9	-1
13	7	12
14	14	15
15	7	11
	$6k3$	
0	70	77
1	14	17
2	<9	-13
3	<10	3
4	54	53
5	38	-41
6	69	70
7	51	-48
8	11	13
9	31	-27
10	11	12
11	<9	-5
12	11	-16
13	<10	1
14	<5	2
	$7k3$	
1	66	63
2	49	-49
3	<10	-10
4	49	-50
5	45	44
6	77	-80
7	<10	-14
8	20	-24
9	13	16
10	14	9
11	16	17
12	<5	-8
13	<4	-2
	$8k3$	
0	70	-67
1	14	-15
2	37	-37
3	<10	5
4	42	45
5	< 9	-10
6	24	21
7	14	-20
8	13	-18
9	16	19
10	<7	-1
11	11	11
12	<4	5
	$9k3$	
1	52	-56
2	23	21
3	11	16
4	20	19
5	15	18
6	<8	0
7	17	-11
8	8	7
9	15	-14
10	10	9
	$10k3$	
0	<7	-10
1	<7	1
2	<7	5
3	8	-8
4	11	-10
5	<6	5
6	28	-22
7	23	21
8	8	-10
	$11k3$	
1	<5	-1
2	15	14
3	<4	6
	$1k\bar{3}$	
1	62	62
2	22	3
3	6	5
4	40	32
5	74	-80
6	132	-133
7	35	-32
8	101	-101
9	28	28
10	44	-34
11	10	-6
12	102	-105
13	12	10
14	45	-50
15	9	9
16	14	-16
17	<5	-3
18	<3	-5
	$2k\bar{3}$	
0	12	6
1	60	-44
2	47	34
3	13	-5
4	44	62
5	65	75
6	76	-88
7	92	96
8	8	-3
9	21	27
0	34	40
1	59	-59
2	<10	14
3	25	-25
14	31	34
15	<9	5
16	22	-20
17	<5	0
	$3k\bar{3}$	
1	95	-92
2	30	-32
3	54	60
4	24	16
5	170	168
6	150	137
7	<8	-14
8	131	115
9	<9	-8
10	8	-13
11	21	-26
12	21	32
13	18	-16
14	32	33
15	10	-5
16	<7	-6
17	28	-28
	$4k\bar{3}$	
0	192	160
1	63	-79
2	77	-81
3	44	-37
4	47	-48
5	60	46
6	19	11
7	116	121
8	18	-13
9	25	-1
10	34	39
11	28	-33
12	43	-42
13	26	29
14	34	-35
15	<8	1
16	14	-13
17	<4	2
	$5k\bar{3}$	
1	140	137
2	97	-83
3	47	-48
4	54	59
5	29	31
6	67	65
7	17	-16
8	17	29
9	12	-12
10	45	-52
11	20	-13
12	26	-28
13	44	-41
14	11	13
15	<7	-3
16	9	15
	$6k\bar{3}$	
0	168	150
1	27	-32
2	119	118
3	17	14
4	75	66
5	<9	-26
6	27	34
7	48	-53
8	10	-3
9	8	11
10	37	-40
11	13	14
12	37	-43
13	<9	-7
14	12	-16
15	<5	-2
16	<3	1
	$7k\bar{3}$	
1	52	52
2	20	-24
3	31	39
4	46	-47
5	71	-77
6	10	-13
7	<10	1
8	27	21
9	12	17
10	41	38
11	15	-10
12	<9	4
13	<8	-5
14	14	-13
15	<4	-6
	$8k\bar{3}$	
0	109	-109
1	35	43
2	28	-19
3	12	15
4	41	-32
5	59	59
6	45	-47
7	85	81
8	<10	-3
9	10	5
10	23	-23
11	<8	10
12	<6	12
13	<5	4
14	<4	5
	$9k\bar{3}$	
1	<8	-1
2	44	37
3	<10	-1
4	14	10
5	28	-28
6	74	68
7	8	-2
8	<9	5
9	20	-21
10	15	-13
11	8	-10
12	<6	4
13	6	-9
	$10k\bar{3}$	
0	83	90
1	18	-24
2	29	32
3	54	-54
4	34	-37
5	<9	2
6	11	-17
7	12	19
8	<8	6
9	17	-16
10	9	10
11	20	-20
	$11k\bar{3}$	
1	19	21
2	25	-21
3	<8	-3
4	<8	5
5	<8	5
6	<7	-3
7	19	16
8	12	-10
9	15	10
	$12k\bar{3}$	
0	<7	-3
1	<7	-8
2	<6	-1
3	<6	5
4	<6	4
5	12	-14
6	8	11

further investigation. With the above co-ordinates for the carbon, nitrogen and oxygen atoms, and approximate scale and temperature factors, a set of three-dimensional structure factors was evaluated. The R-factor was 19·7%. A difference synthesis calculated from these terms confirmed the x and y co-ordinates of the hydrogen atoms and indicated z values. These atoms were assigned an isotropic temperature factor of 3·8 Å^2. Other maxima were in accordance with a small anisotropy of the molecule and approximate B coefficients were found for the temperature-factor expression

$$2^{-(B_{11}h^2+B_{22}k^2+B_{33}l^2+B_{12}hk+B_{23}kl+B_{31}lh)}$$

The least-squares programme refines these coefficients together with the atomic co-ordinates and scale factor. The difficulty in correlating the separate layer lines was overcome by scaling each to the calculated value. This was repeated for two cycles when the factors became constant. In the seven cycles of least-squares refinement, adjustments were made to the overall scale factor, and to the co-ordinates and temperature factors of the carbon, nitrogen and oxygen atoms only. Because of the incompleteness of the data, it was deemed unwise to take the magnitude of the shifts for the temperature factors; only the direction was

Table 2. *The fractional co-ordinates referred to the monoclinic crystal axes*

Atom	x	y	z
C_2	0·1172	0·1124	0·2696
C_4	−0·0888	0·0349	0·2240
C_5	−0·0281	−0·0460	0·2507
C_6	0·1134	−0·0535	0·2891
C_8	−0·2480	−0·0723	0·1926
C_{10}	0·3261	0·0310	0·3322
C_{12}	−0·0873	0·2029	0·2126
C_{14}	−0·1084	−0·2094	0·2384
C_{16}	−0·3385	0·0849	0·1564
N_1	0·1786	0·0301	0·2966
N_3	−0·0217	0·1141	0·2341
N_7	−0·1259	−0·1123	0·2306
N_9	−0·2248	0·0208	0·1895
O_{11}	0·1827	0·1810	0·2825
O_{13}	0·1779	−0·1245	0·3125
O_{15}	−0·3599	−0·1070	0·1622
H_1	−0·150	0·217	0·333
H_2	−0·100	0·212	0·050
H_3	−0·022	0·255	0·267
H_4	−0·417	0·056	0·167
H_5	−0·283	0·090	0·067
H_6	−0·345	0·133	0·233
H_7	0·375	0·075	0·400
H_8	0·377	−0·013	0·271
H_9	0·342	−0·027	0·425
H_{10}	−0·167	−0·250	0·183
H_{11}	−0·033	−0·237	0·333
H_{12}	−0·050	−0·216	0·140

considered. These shifts, which would undoubtedly give better agreement between observed and calculated structure factors, would lead to pronounced anisotropy of some of the atoms, thought to be meaningless. At the end of the seventh cycle when changes in atomic co-ordinates were less than the standard deviations, refinement was terminated. The R-factor for the observed reflexions is 11·2%. Observed and calculated structure factors are listed in Table 1, and atomic co-ordinates in Table 2. The standard deviations in the co-ordinates calculated using the weighted residuals from the least-squares refinement are

$$\sigma(x) = 0{\cdot}007,\ 0{\cdot}005,\ 0{\cdot}004\ \text{Å}$$
$$\sigma(y) = 0{\cdot}007,\ 0{\cdot}005,\ 0{\cdot}004$$
$$\sigma(z) = 0{\cdot}009,\ 0{\cdot}007,\ 0{\cdot}006$$

for carbon, nitrogen and oxygen atoms respectively.

Bond lengths and bond angles are given in Tables 3 and 4. The estimated standard deviations are 0·011 Å in C–C, 0·010 Å in C–N and 0·009 Å in C–O bonds.

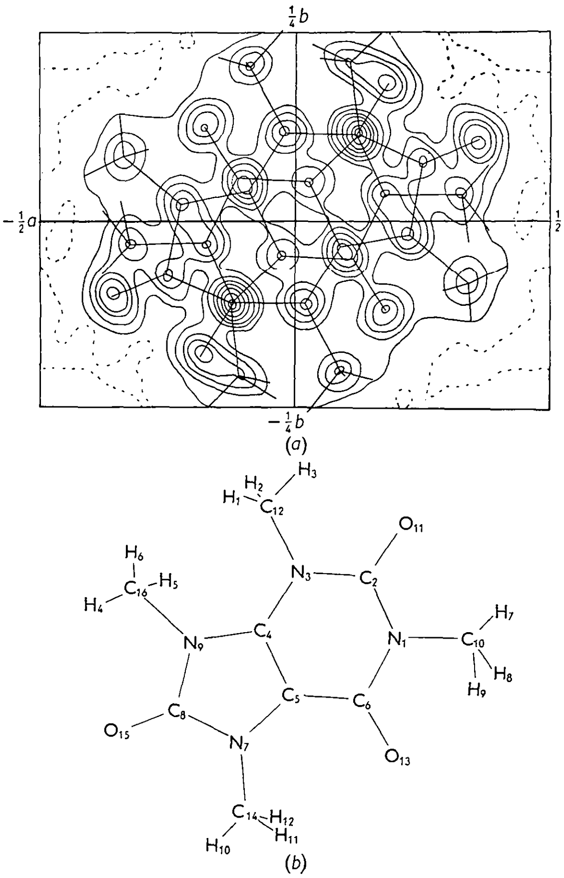

Fig. 1. (a) $hk0$ Fourier projection calculated using the final structure factors from the three dimensional refinement. Contours are at intervals of 2 e.Å^{-2} with the zero contour broken. The origin is at the centre. (b) 1,3,7,9-Tetramethyluric acid showing the positions of all the atoms and the numbering system used.

Table 3. *Comparison of bond lengths and bond angles in theophylline, caffeine and tetramethyluric acid*

(a) *Bond lengths*

Bond	Theophylline	Caffeine	Tetramethyl-uric acid
C_4–C_5	1·37 Å	1·32 Å	1·349 Å
C_5–C_6	1·41	1·44	1·412
C_2–N_1	1·40	1·42	1·369
C_2–N_3	1·35	1·35	1·387
C_4–N_3	1·37	1·42	1·356
C_6–N_1	1·38	1·36	1·405
C_4–N_9	1·33	1·31	1·369
C_8–N_9	1·31	1·34	1·407
C_8–N_7	1·31	1·32	1·353
C_5–N_7	1·34	1·41	1·386
C_{10}–N_1	1·48	1·48	1·467
C_{12}–N_3	1·46	1·50	1·474
C_{14}–N_7	—	1·47	1·456
C_{16}–N_9	—	—	1·480
C_2–O_{11}	1·19	1·19	1·209
C_6–O_{13}	1·22	1·26	1·237
C_8–O_{15}	—	—	1·227

(b) *Bond angles*

An atom followed by (H) should be replaced by hydrogen where indicated

Angle	Theophylline	Caffeine	Tetramethyl-uric acid
C_2–N_1–C_6	126·0°	127·6°	126·3°
C_2–N_1–C_{10}	115·7	112·0	115·7
C_6–N_1–C_{10}	117·7	120·3	118·1
N_1–C_2–N_3	117·8	112·9	117·3
N_1–C_2–O_{11}	120·8	122·7	121·4
N_3–C_2–O_{11}	121·8	124·1	121·3
C_2–N_3–C_4	119·4	122·8	118·5
C_2–N_3–C_{12}	119·6	117·9	117·3
C_4–N_3–C_{12}	121·1	119·2	124·2
N_3–C_4–C_5	121·8	121·4	124·0
N_3–C_4–N_9	125·5	127·2	128·3
C_5–C_4–N_9	112·7	110·9	107·7
C_4–C_5–C_6	122·6	119·9	121·1
C_4–C_5–N_7	104·2	107·2	108·9
C_6–C_5–N_7	133·1	132·8	130·0
N_1–C_6–C_5	112·5	115·8	112·9
N_1–C_6–O_{13}	121·2	118·4	121·3
C_5–C_6–O_{13}	126·5	126·4	125·8
C_5–N_7–C_8	106·7	103·4	108·4
C_5–N_7–C_{14}(H)	135·0 (H)	128·7	128·6
C_8–N_7–C_{14}(H)	118·0 (H)	127·5	123·0
N_7–C_8–N_9	114·3	112·3	106·7
N_7–C_8–O_{15}(H)	121·0 (H)	112·0 (H)	129·0
N_9–C_8–O_{15}(H)	125·0 (H)	135·0 (H)	124·3
C_4–N_9–C_8	102·0	105·7	108·3
C_4–N_9–C_{16}	—	—	131·0
C_8–N_9–C_{16}	—	—	120·7

Table 4. *The* C–H *bond lengths*

Bond	Bond length	Bond	Bond length
C_{10}–H_7	0·9 Å	C_{14}–H_{10}	0·9 Å
C_{10}–H_8	1·0	C_{14}–H_{11}	1·0
C_{10}–H_9	1·1	C_{14}–H_{12}	1·0
C_{12}–H_1	1·1	C_{16}–H_4	0·9
C_{12}–H_2	1·1	C_{16}–H_5	0·9
C_{12}–H_3	1·0	C_{16}–H_6	0·9

Angles have a standard deviation of about 0·7° calculated from the formula of Cruickshank & Robertson (1953).

The least-squares, normal equation of the plane containing the carbon, nitrogen and oxygen atoms is

$$-0{\cdot}1765x+0{\cdot}0406y+0{\cdot}9835z-1{\cdot}6958=0$$

where x, y and z are the co-ordinates (in Å) referred to the orthogonal axes a, b and c'. The average deviation of atoms from this plane is 0·013 Å. The plane of the ring atoms only is given by

$$-0{\cdot}1797x+0{\cdot}0518y+0{\cdot}9824z-1{\cdot}6990=0\ ,$$

and the average deviation of these atoms is 0·004 Å. Table 5 lists the displacements of atoms from these two planes. The deviations from the second plane indicate that the purine group is strictly planar with attached atoms in half the molecule above and in the other half below the plane, except for O_{11} and O_{13} whose deviations are not significant. However, as the average deviation of atoms from the molecular plane is only 0·013 Å, maximum 0·024 Å, it is doubtful whether any of these displacements are significant and therefore the molecule can be taken as being planar.

Table 5. *Distance of atoms from (a) the molecular plane, (b) the plane of the purine group whose atoms are starred*

Atom	(a) (Å)	(b) (Å)
C_2	−0·020	−0·009*
C_4	−0·006	−0·001*
C_5	0·017	0·007*
C_6	0·019	0·003*
C_8	0·002	−0·006*
C_{10}	−0·018	−0·028
C_{12}	0·016	0·049
C_{14}	−0·021	−0·056
C_{16}	0·014	0·036
N_1	0·004	−0·001*
N_3	−0·009	0·006*
N_7	0·016	−0·002*
N_9	−0·004	0·003*
O_{11}	−0·007	0·013
O_{13}	0·019	−0·011
O_{15}	−0·024	−0·034

Discussion of the structure

Intramolecular distances

For comparative purposes, Table 3 gives the bond lengths and angles in theophylline, caffeine and tetramethyluric acid. In the comparison of molecular dimensions, the significance tests of Cruickshank & Robertson (1953) were used, and any difference greater than, or equal to 2·5σ has been assumed real. The following discussion shows that the dimensions of the rings are dependent on the presence and nature of substituents.

All three purines have about 1·38 Å for the average of the C–N bonds in the completely substituted pyrimidine ring. The average length of C–N bonds in the five-membered ring—1·32 Å for theophylline, 1·35 Å for caffeine and 1·38 Å for tetramethyluric acid—increases as carbon and oxygen atoms are introduced, and finally reaches 1·38 Å on complete substitution. In tetramethyluric acid, all C–N bonds of the five-membered ring are significantly longer than corresponding bonds in theophylline. The shortening of the C_2–N_3 bond observed in adenine hydrochloride (Cochran, 1951), as well as in theophylline and caffeine, has disappeared here.

Exocyclic C–N bonds average 1·469 Å, in good agreement with the single bond value of 1·47 Å. The average of the C=O bonds, 1·224 Å, is not significantly different from their average in theophylline, 1·205 Å, or from the double bond value of 1·20 Å.

There is a striking similarity between the bond angles at N_1 and C_2 for theophylline and tetramethyluric acid, but other angles appear to be affected by the presence of extra methyl and oxygen substituents in the latter. Steric hindrance between O_{13} and C_{14} of adjacent rings has caused these two atoms to move away from each other, and a similar but more pronounced effect exists between the two methyl groups C_{12} and C_{16}. Evidence for this lies in the inequality of pairs of exocyclic angles at C_6, N_7, N_3 and N_9. The same steric effect has been observed in caffeine and probably theophylline where a hydrogen atom is involved. In all three purines, the bond angle C_2–N_3–C_4 is significantly less than C_2–N_1–C_6, possibly a feature of the methyl hydroxy purines.

The dimensions of the pyrimidine ring are similar to Spencer's values (1959) obtained by averaging like bonds in known pyrimidine and purine structures. Discrepancies occur in the N_1–C_6 bond value which in tetramethyluric acid is significantly longer than the predicted value and longer than that found in caffeine and probably theophylline, and in the bond angles particularly C_2–N_3–C_4 which in these methyl hydroxy purines appears to be significantly smaller than the other C–N–C angle. The predicted C=O bond length, 1·22 Å, agrees well with the observed values.

Anisotropic vibration

In Table 6, the maximum, intermediate and minimum values of the axes of the vibration ellipsoids, and their angles referred to the orthogonal axes, a, b and c' are given. No errors can be quoted for suggested shifts in the temperature coefficients are still greater than the standard deviations. The anisotropic vibration of the molecules can be explained in terms of the oscillation of the atoms about the molecular centre. For most atoms, the direction of maximum vibration lies in the molecular plane perpendicular to the bond formed externally to the ring. Most ring atoms have the minimum axis of the vibration ellipsoid perpendicular to the plane, but

Table 6. *Anisotropic temperature factors*

The B values for the axes of the vibration ellipsoids and their angles with respect to the orthogonal axes a, b and c' are given

Atom	B (Å^2)	Angle with a (°)	Angle with b (°)	Angle with c' (°)
C_2	3·7	63	149	104
	3·2	124	94	146
	2·5	47	59	121
C_4	3·5	67	154	78
	3·0	118	112	143
	2·4	38	77	125
C_5	3·8	81	171	87
	3·1	13	81	81
	1·9	100	89	10
C_6	3·8	60	44	119
	3·3	36	102	58
	3·0	107	49	46
C_8	5·0	69	159	87
	3·8	24	69	81
	2·0	81	90	171
C_{10}	5·5	92	10	100
	3·6	82	99	168
	2·8	9	87	82
C_{12}	4·8	26	69	76
	4·2	99	107	19
	3·1	115	28	78
C_{14}	5·2	38	100	127
	4·3	125	81	144
	3·0	103	167	92
C_{16}	5·2	94	123	33
	4·9	79	36	57
	2·7	12	102	93
N_1	4·1	92	177	88
	2·9	20	91	70
	1·7	110	87	20
N_3	3·2	25	71	74
	3·0	71	161	88
	2·1	106	94	17
N_7	4·0	39	114	119
	3·4	113	74	151
	3·0	119	151	95
N_9	4·0	95	171	98
	3·0	10	96	82
	2·2	99	97	12
O_{11}	4·7	50	136	107
	3·8	127	104	140
	3·5	62	49	125
O_{13}	4·6	48	52	113
	4·3	80	69	24
	3·5	45	134	83
O_{15}	5·2	74	164	86
	4·2	79	91	169
	3·6	19	74	80

exocyclic atoms, which have a greater freedom of movement, have the intermediate value in this direction. This out-of-plane vibration is more pronounced in the case of C_{14} and C_{16}. Under the circumstances, no quantitative analysis of the thermal parameters is possible, but as expected, exocyclic atoms have larger B values than atoms in the ring, an effect which is particularly noticeable for the methyl groups.

Intermolecular distances

Molecules are stacked in parallel planes almost perpendicular to the c axis and of alternate spacing 3·39 and 3·36 Å. The closest approach distances between layers are $C_4 \cdots C_6' = 3{\cdot}44$, 3·35 Å, $C_2 \cdots N_7' = 3{\cdot}39$, 3·36 Å with atoms below and above respectively. These blocks of molecules are related by screw axes. In the other form of tetramethyluric acid, this close packing is not maintained. Instead there are pairs of molecules in parallel planes 3·5 Å apart with adjacent pairs practically at right angles to each other.

Table 7. *Intermolecular distances between exocyclic atoms less than 4·5 Å apart*

Atom in reference molecule at x, y, z	Atom in neighbouring molecule	Intermolecular distance
C_{10}	$C_{10}(1-x, -y, 1-z)$	3·93 Å
	$C_{12}(\frac{1}{2}+x, \frac{1}{2}-y, z)$	4·17
	$C_{16}(-x, -y, -z)$	3·74
	$C_{16}(-x, -y, 1-z)$	3·84
	$C_{16}(1+x, y, z)$	3·87
C_{12}	$C_{14}(-x, -y, 1-z)$	3·87
	$C_{14}(-x, -y, -z)$	3·92
	$C_{14}(-\frac{1}{2}-x, \frac{1}{2}+y, -z)$	4·13
	$C_{16}(\frac{1}{2}+x, \frac{1}{2}-y, z)$	4·10
C_{14}	$C_{16}(-\frac{1}{2}-x, -\frac{1}{2}+y, -z)$	4·03
C_{16}	$C_{16}(-1-x, -y, -z)$	4·36
C_{10}	$O_{15}(1+x, y, z)$	4·11
	$O_{15}(-x, -y, 1-z)$	3·55
	$O_{15}(-x, -y, -z)$	3·60
C_{12}	$O_{11}(-\frac{1}{2}+x, \frac{1}{2}-y, z)$	3·00
	$O_{13}(-x, -y, 1-z)$	3·68
	$O_{13}(-x, -y, -z)$	3·69
	$O_{15}(-\frac{1}{2}-x, \frac{1}{2}+y, -z)$	3·77
C_{14}	$O_{11}(-x, -y, 1-z)$	3·48
	$O_{11}(-x, -y, -z)$	3·49
	$O_{13}(-\frac{1}{2}+x, -\frac{1}{2}-y, z)$	3·38
	$O_{15}(\frac{1}{2}+x, -\frac{1}{2}-y, z)$	3·81
C_{16}	$O_{11}(-\frac{1}{2}+x, \frac{1}{2}-y, z)$	3·59
	$O_{13}(-x, -y, 1-z)$	3·71
	$O_{13}(-x, -y, -z)$	3·85
	$O_{15}(-1-x, -y, -z)$	3·42
O_{11}	$O_{13}(\frac{1}{2}-x, \frac{1}{2}+y, 1-z)$	4·06
	$O_{15}(-x, -y, 1-z)$	4·01
	$O_{15}(-x, -y, -z)$	3·92
O_{13}	$O_{15}(\frac{1}{2}+x, -\frac{1}{2}-y, z)$	4·13

All intermolecular distances between exocyclic atoms less than 4·5 Å apart are given in Table 7 and some of the shorter intermolecular contacts are shown in Fig. 2. The average $CH_3 \cdots CH_3$ separation, 4·00 Å, agrees with Pauling's value of 4·00 Å for the sum of the van der Waals radii, but $O \cdots O$ distances appear to be long. Two of the $CH_3 \cdots O$ lengths (3·00, 3·38 Å) are less than 3·4 Å, the sum of the van der Waals radii of methyl and oxygen, the first being much shorter than similar contacts of 3·24 Å and $CH \cdots O$ distances of 3·22 and 3·18 Å in theophylline and caffeine. Such a close contact might lead to speculation as to the correctness of the proposed atomic arrangement, but there are no other disturbing features such as outstanding disagreement between certain observed and calculated structure factors, spurious maxima in difference or Fourier syntheses, or chemical incompatibility. The co-ordinates have refined satisfactorily, hence there cannot be large errors in x and y, and the molecular geometry and arrangement is such that the $CH_3 \cdots O$ distance is practically independent of the less accurate z values. Other positions for the molecule as suggested by the $hk0$ Patterson function were investigated but none of these would refine. It is therefore concluded that the proposed arrangement does not represent a homometric structure.

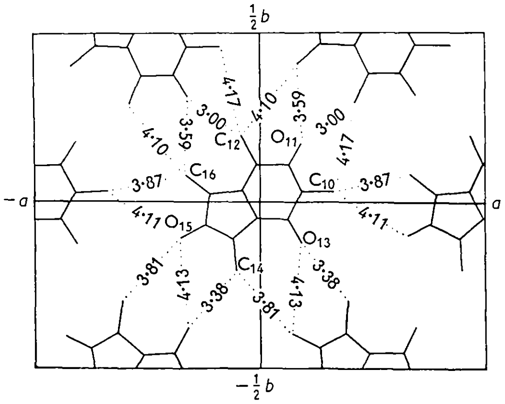

Fig. 2. Some of the intermolecular contacts in a layer of the structure.

A search of the literature shows that 'short' intermolecular contacts of this type are not uncommon though frequently their significance is not investigated; though common among the pyrimidines and purines, they are by no means confined to them. A survey will be published later, but a few examples are given here. As well as those in caffeine and theophylline (3·24 Å), there is an intramolecular $CH_3 \cdots O$ contact of 2·87 Å in muscarine iodide (Jellinek, 1957), the methyl group again being attached to a nitrogen atom. Many other 'short' $CH \cdots O$ distances are known, e.g. 3·19 and 3·28 Å in uracil (Parry, 1954), and 3·24 Å (intramolecular) in cytidine (Furberg, 1950). These could well represent examples of what is regarded as an uncommon $C–H \cdots O$ hydrogen bond. It is well known that a carbon atom may use its hydrogen atom in hydrogen-bond formation if another more electronegative atom is attached to it, thus causing activation of the C–H group. Dulmage & Lipscomb (1951) have shown that hydrogen cyanide at −120 and −80 °C. consists of linear chains of molecules with 'short' distances between the carbon and nitrogen atoms in the direction $C–H \cdots N$. These contacts appear to be hydrogen bonds. Activation of the C–H group can occur in tetramethyluric acid and is enhanced by the electrophilic nature of the keto grouping. The relevant bond lengths and angles in this probable hydrogen bond are shown in Fig. 3.

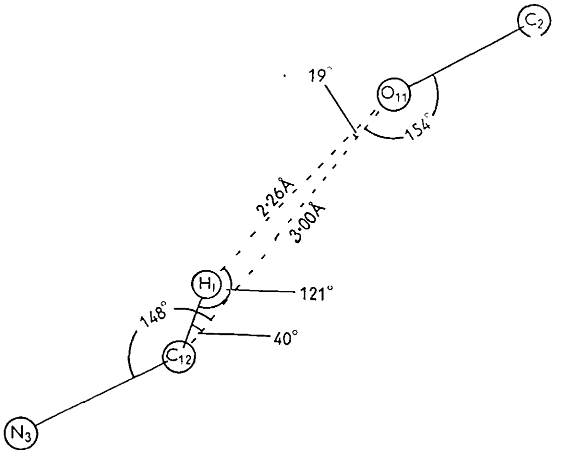

Fig. 3. The distances and angles in the 'short' intermolecular contact.

It is not yet possible to make a detailed comparison with the other form, though some general conclusions can be drawn. The smaller volume of the unit cell of this form is the result of a more economical packing of the molecules with shorter interplanar spacings and presumably other shorter intermolecular contacts. The fact that no 'forbidden' reflexions were observed points to this closely-bonded ordered array of molecules. The polymorphic change in tetramethyluric acid evidently represents the rearrangement of an ordered lattice described here into a disordered one in the other form.

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