The Crystal and Electronic Structure of Isocoffeine,

(1,3,9-Trimethyl-2,6-dioxypurine)

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The crystal structure of 1,3,9-trimethyl-2,6-dioxypurine has been determined by X-ray diffraction methods. The structure was determined from three-dimensional diffractometer data and refined to $R = 0.039$ including 1720 reflections. Standard deviations in bond lengths involving only non-hydrogen atoms are approximately 0.002 Å and for those involving hydrogen atoms 0.02 Å. The corresponding standard deviations in angles are 0.1° and 1°, respectively. The methyl group in 9-position is nearly eclipsed relative to the methyl group on N(3) and to the hydrogen atom on C(8). The purine molecule is slightly, though significantly, bent around the C(4)−C(5) bond. The carbonyl group C(2)−O(2) is displaced out of the pyrimidine plane by about 0.04 Å for C(2) and 0.08 Å for O(2).

B ergmann and coworkers have carried out extensive conformational studies on substituted purines in solutions by spectroscopic and dielectric measurements.[1,2] Some of the problems encountered in these investigations could possibly be clarified by X-ray diffraction methods. The first compound in this series is the isocoffeine molecule (1,3,9-trimethyl-2,6-dioxypurine) where the steric interaction between the 3- and 9-methyl groups is of particular interest.

EXPERIMENTAL

A sample of 1,3,9-trimethyl-2,6-dioxypurine was kindly supplied by F. Bergmann. The compound was crystallized from chloroform by slow evaporation in a refrigerator. A fairly large crystal with dimensions $0.71 \times 0.34 \times 0.33$ mm³ was mounted along the a^*-axis and used for intensity measurements. The space group is $P2_1/n$, $Z = 4$, with cell dimensions $a = 7.717(2)$ Å, $b = 7.915(5)$ Å, $c = 13.646(2)$ Å, $\beta = 92.86(1)°$, $\varrho_{obs} = 1.54(1)$ g cm⁻³, $\varrho_{calc} = 1.549(3)$ g cm⁻³.

Three-dimensional data were collected on a Siemens AED four-circle diffractometer using niobium-filtered MoKα radiation. Within a sphere limited at sin $\theta/\lambda < 0.64$, 1813 reflections were measured with $\theta - 2\theta$ scan employing the 5-value measurement procedure. All measurements start at the reflection peak to enable the instrument to test the maximum counting rate and automatically insert an appropriate attenuator in the

primary beam to avoid counting losses, or to select an appropriate measuring time per step to give a statistically suitable count. Except for the very weak reflections which are recorded with a constant maximum scan time, all the reflections are measured at approximately the same statistical accuracy. The X-ray tube was operated at 50 kV, 20 mA, except for the measurements of nine very strong low order reflections which had to be recorded with the minimum current setting of 8 mA. During the collection of data two standard reflections were re-measured after each set of 50 reflections. The fluctuations in net intensities were about ± 1 % with one single deflection for both standards of about 6 %. Lorentz and polarization corrections were applied to the intensity data. The linear absorption coefficient for the compound is 1.24 cm^{-1} and no absorption correction was deemed necessary.

STRUCTURE DETERMINATION AND REFINEMENT

The structure was solved by a symbolic addition procedure programmed by Long.[3] Three origin determining reflections and three reflections with variable signs were used in the initial phasing process. 102 normalized structure factors with $E > 2.0$ were used for sign determinations. In addition, signs were derived for reflections with E-values in the range $1.5 - 2.0$. The total number of reflections used in the process were 243.

An E map based on the set of phases with highest consistency revealed all non-hydrogen atoms unambiguously. Structure factor calculations based on the coordinates of these atoms gave an R-factor of 0.32. Three cycles of least-squares refinement lowered R to 0.12. The hydrogen atoms were localized by three-dimensional difference synthesis. Two more refinement cycles using anisotropic temperature factors on non-hydrogen atoms and isotropic temperature factors on hydrogen atoms gave $R = 0.048$.

Correction for secondary extinction was carried out according to the formula given by Zachariasen.[4] Four very strong low order reflections which had been measured far outside the linear range of the counter had large ΔF's and were given zero weight in the two final refinement cycles. At this stage all shifts were less than 0.1 σ and the refinement was terminated at an R of 0.039.

The final atomic coordinates and thermal parameters along with the corresponding standard deviations are shown in Tables 1 and 2. Table 3 lists the observed and calculated structure factors. Atomic scattering factors for the heavier atoms were obtained from *International Tables for X-Ray Crystallography* (1962),[5] and those for the hydrogen atoms were from Stewart, Davidson and Simpson.[6]

A residual difference synthesis based on all atoms showed peaks of electron densities 0.1 to 0.25 eÅ^{-3} approximately in the middle of the bonds. As in previous published purine structures the largest peak appears in the middle of the conjugated bond $C(4) - C(5)$.

THERMAL ANALYSIS

The thermal parameters were used in a rigid body motion analysis [7] in which the xanthine part of the molecule was assumed to form the rigid body. The root-mean-square amplitudes about principal axes of librational motion are 23.1°, 8.5°, 6.5°, respectively. The root-mean-square deviation between

Table 1. Final positional parameters with the corresponding standard deviations in parentheses.

Atom	X/a	Y/b	Z/c
C(1)	0.06913(24)	0.77805(21)	0.12922(13)
C(2)	0.19287(19)	0.49956(19)	0.10826(10)
C(3)	0.30248(27)	0.21269(21)	0.09372(14)
C(4)	0.30084(18)	0.42132(18)	− 0.04456(10)
C(5)	0.26343(19)	0.57569(18)	− 0.08501(10)
C(6)	0.18436(20)	0.70455(18)	− 0.03064(10)
C(8)	0.37536(23)	0.43245(21)	− 0.19597(11)
C(9)	0.43771(25)	0.15407(22)	− 0.11628(14)
N(1)	0.15080(16)	0.65437(15)	0.06555(8)
N(3)	0.26569(16)	0.37863(15)	0.04999(8)
N(7)	0.31193(18)	0.58181(18)	− 0.18122(9)
N(9)	0.37463(17)	0.32783(16)	− 0.11543(9)
O(2)	0.16437(16)	0.47178(15)	0.19360(8)
O(6)	0.14618(18)	0.84710(14)	− 0.05904(8)
H(8)	0.4282(27)	0.3879(26)	− 0.2580(15)
H(11)	0.0128(25)	0.8695(25)	0.0884(15)
H(12)	0.1530(27)	0.8355(26)	0.1797(15)
H(13)	− 0.0150(28)	0.7236(26)	0.1723(17)
H(31)	0.2508(34)	0.2088(32)	0.1550(22)
H(32)	0.4349(34)	0.1945(30)	0.1117(18)
H(33)	0.2578(30)	0.1279(31)	0.0584(17)
H(91)	0.5233(28)	0.1378(25)	− 0.0632(15)
H(92)	0.3552(28)	0.0728(27)	− 0.1086(15)
H(93)	0.4720(28)	0.1285(28)	− 0.1798(17)

Table 2. Thermal parameters with the corresponding standard deviations in parentheses. The anisotropic thermal parameters are defined by the expression
$$T_i = \exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)]$$
and the isotropic parameters by $T_i = \exp[-8\pi^2 U \sin^2 \theta/\lambda^2]$. For non-hydrogen atoms the values are multiplied by a factor of 10^4, for hydrogen atoms by 10^3.

	U_{11}	U_{22}	U_{33}	U_{12}	U_{23}	U_{13}
C(1)	424(9)	317(8)	340(8)	49(7)	− 77(7)	53(7)
C(2)	295(7)	297(8)	249(7)	− 3(6)	9(6)	29(5)
C(3)	579(12)	253(8)	336(9)	50(8)	68(7)	43(8)
C(4)	260(7)	256(7)	234(7)	− 15(6)	− 19(5)	16(5)
C(5)	328(8)	275(7)	237(7)	− 18(6)	24(6)	39(6)
C(6)	324(8)	251(7)	279(7)	− 24(6)	18(6)	13(6)
C(8)	447(9)	395(9)	253(7)	− 18(7)	− 13(6)	85(6)
C(9)	417(10)	310(9)	393(9)	58(7)	− 79(7)	55(8)
N(1)	321(7)	253(6)	257(6)	16(5)	− 24(5)	35(5)
N(3)	356(7)	238(6)	236(6)	20(5)	29(5)	40(5)
N(7)	488(8)	374(7)	247(6)	− 10(6)	32(5)	75(6)
N(9)	335(7)	296(7)	264(6)	− 1(5)	− 34(5)	53(5)
O(2)	579(8)	448(7)	247(6)	89(6)	53(5)	115(5)
O(6)	658(9)	256(6)	418(7)	77(6)	77(5)	73(6)

	U		U		U
H(8)	53(6)	H(31)	83(8)	H(91)	52(6)
H(11)	52(6)	H(32)	76(7)	H(92)	51(6)
H(12)	55(6)	H(33)	68(7)	H(93)	61(6)
H(13)	56(6)				

Table 3. Observed and calculated structure factors multiplied by 10. Unobserved reflections are marked with a minus sign in front of F_o.

H	K	L	F(O)	F(C)
0	0	2	690	669
0	0	4	613	-661
0	0	6	350	-342
0	0	8	469	-450
0	0	10	96	109
0	0	12	202	-209
0	0	14	155	-162
0	0	16	122	121
0	1	1	859	-802
0	1	2	151	154
0	1	3	370	354
0	1	4	266	-268
0	1	5	304	-301
0	1	6	468	-453
0	1	7	312	297
0	1	8	94	-88
0	1	9	103	89
0	1	10	155	154
0	1	11	115	-113
0	1	12	20	-24
0	1	13	181	184
0	1	14	138	-111
0	1	15	22	-17
0	1	16	-10	-1
0	1	17	-11	-6
0	2	0	47	-49
0	2	1	89	85
0	2	2	450	-454
0	2	3	167	-160
0	2	4	209	200
0	2	5	274	-265
0	2	6	148	150
0	2	7	68	67
0	2	8	262	-258
0	2	9	9	-9
0	2	10	161	162
0	2	11	71	71
0	2	12	24	16
0	2	13	103	105
0	2	14	45	-46
0	2	15	-10	2
0	2	16	28	28
0	2	17	-11	4
0	3	1	193	-191
0	3	2	175	-168
0	3	3	390	390
0	3	4	145	148
0	3	5	44	41
0	3	6	25	23
0	3	7	89	91
0	3	8	8	-7
0	3	9	99	-102
0	3	10	101	105
0	3	11	116	-115
0	3	12	27	29
0	3	13	57	55
0	3	14	28	-26
0	3	15	27	-26
0	3	16	-10	-1
0	4	0	309	-290
0	4	1	241	236
0	4	2	310	-295
0	4	3	240	227
0	4	4	80	-74
0	4	5	9	14
0	4	6	152	149
0	4	7	84	-83
0	4	8	205	208
0	4	9	257	-261
0	4	10	193	190
0	4	11	113	-113
0	4	12	-10	11
0	4	13	56	54
0	4	14	28	-22
0	4	15	-11	7
0	5	1	120	115
0	5	2	170	-163
0	5	3	25	-24
0	5	4	80	81
0	5	5	33	-34
0	5	6	152	148
0	5	7	86	-86
0	5	8	150	153
0	5	9	125	-124
0	5	10	42	42
0	5	11	-10	6
0	5	12	116	-112
0	5	13	46	42
0	5	14	51	-47
0	5	15	28	26
0	6	0	105	104
0	6	1	29	29
0	6	2	101	100
0	6	3	32	-33
0	6	4	104	-105
0	6	5	-9	2
0	6	6	128	-128
0	6	7	76	74
0	6	8	77	81
0	6	9	31	35
0	6	10	14	13
0	6	11	11	10
0	6	12	52	-52
0	6	13	17	-15
0	6	14	13	8
0	7	1	53	52
0	7	2	54	58
0	7	3	47	45
0	7	4	55	55
0	7	5	133	139
0	7	6	56	-58
0	7	7	44	-44
0	7	8	21	-20
0	7	9	84	-89
0	7	10	13	13
0	7	11	14	11
0	7	12	-11	-9
0	8	0	57	-61
0	8	1	30	-31
0	8	2	15	16
0	8	3	109	-107
0	8	4	-10	0
0	8	5	60	-60
0	8	6	18	-19
0	8	7	33	-34
0	8	8	27	27
0	8	9	25	-24
0	8	10	52	-46
0	9	1	-10	4
0	9	2	25	23
0	9	3	65	-65
0	9	4	15	16
0	9	5	25	-26
0	9	6	64	-59
0	9	7	-10	-5
0	10	0	-11	-4
0	10	1	41	42
0	10	2	-11	7
1	0	-17	24	-19
1	0	-15	66	62
1	0	-13	12	10
1	0	-11	104	-104
1	0	-9	214	-227
1	0	-7	218	-239
1	0	-5	-7	12
1	0	-3	207	225
1	0	-1	-5	-15
1	0	1	145	141
1	0	3	224	225
1	0	5	124	131
1	0	7	66	67
1	0	9	55	-60
1	0	11	32	-34
1	0	13	121	126
1	0	15	45	46
1	0	17	-10	1
1	1	-17	32	-30
1	1	-16	37	34
1	1	-15	10	-9
1	1	-14	73	79
1	1	-13	90	95
1	1	-12	40	46
1	1	-11	88	88
1	1	-10	75	-76
1	1	-9	123	-129
1	1	-8	-7	-7
1	1	-7	53	-44
1	1	-6	11	-4
1	1	-5	229	237
1	1	-4	65	-60
1	1	-3	232	243
1	1	-2	27	-34
1	1	-1	119	113
1	1	0	52	49
1	1	1	35	-40
1	1	2	-6	-11
1	1	3	108	120
1	1	4	202	221
1	1	5	41	40
1	1	6	59	59
1	1	7	61	-59
1	1	8	83	-85
1	1	9	170	-175
1	1	10	25	-25
1	1	11	91	-92
1	1	12	69	-71
1	1	13	72	74
1	1	14	78	-81
1	1	15	82	79
1	1	16	11	-14
1	1	17	18	17
1	2	-17	-11	-2
1	2	-16	34	31
1	2	-15	79	-79
1	2	-14	22	-26
1	2	-13	24	-27
1	2	-12	276	-287
1	2	-11	201	199
1	2	-10	227	-224
1	2	-9	189	185
1	2	-8	33	-37
1	2	-7	-7	9
1	2	-6	100	94
1	2	-5	115	-115
1	2	-4	366	370
1	2	-3	160	-150
1	2	-2	185	176
1	2	-1	123	-123
1	2	0	134	133
1	2	1	74	-76
1	2	2	-6	10
1	2	3	7	-4
1	2	4	38	-37
1	2	5	71	-78
1	2	6	52	-54
1	2	7	-9	-14
1	2	8	65	-68
1	2	9	40	43
1	2	10	37	-35
1	2	11	58	-57
1	2	12	108	-109
1	2	13	21	-20
1	2	14	29	-30
1	2	15	-10	10
1	2	16	62	59
1	3	-16	23	-22
1	3	-15	52	-54
1	3	-14	29	-24
1	3	-13	90	90
1	3	-12	169	-173
1	3	-11	244	248
1	3	-10	153	-153
1	3	-9	48	43
1	3	-8	78	88
1	3	-7	41	-42
1	3	-6	245	228
1	3	-5	281	-268
1	3	-4	362	346
1	3	-3	137	-128
1	3	-2	86	-84
1	3	-1	125	122
1	3	0	106	-109
1	3	1	310	-314
1	3	2	191	196
1	3	3	206	-205
1	3	4	213	-219
1	3	5	162	-158
1	3	6	225	-222
1	3	7	9	-12
1	3	8	114	-12
1	3	9	60	60
1	3	10	109	108
1	3	11	137	133
1	3	12	236	240
1	3	13	175	174
1	3	14	63	60
1	3	15	-10	-1
1	3	16	32	-30
1	4	-15	42	-40
1	4	-14	35	31
1	4	-13	35	-36
1	4	-12	48	48
1	4	-11	102	107
1	4	-10	45	48
1	4	-9	10	-3
1	4	-8	79	-77
1	4	-7	18	-9
1	4	-6	139	-138
1	4	-5	167	-155
1	4	-4	195	180
1	4	-3	147	-138
1	4	-2	76	74
1	4	-1	381	372
1	4	0	111	112
1	4	1	185	-186
1	4	2	86	83
1	4	3	261	-267
1	4	4	179	180
1	4	5	168	166
1	4	6	199	203
1	4	7	215	210
1	4	8	85	-87
1	4	9	193	193
1	4	10	93	-98
1	4	11	102	-104
1	4	12	120	-119
1	4	13	141	-143
1	4	14	67	-69
1	4	15	23	27
1	5	-15	30	-27
1	5	-14	59	58
1	5	-13	-10	0
1	5	-12	46	-44
1	5	-11	20	-25
1	5	-10	69	73
1	5	-9	22	19
1	5	-8	157	160
1	5	-7	271	272
1	5	-6	78	-77
1	5	-5	11	-15
1	5	-4	79	82
1	5	-3	193	-188
1	5	-2	46	-48
1	5	-1	129	-124
1	5	0	122	-118
1	5	1	-7	-10
1	5	2	61	59
1	5	3	103	104
1	5	4	212	-222
1	5	5	159	-152
1	5	6	26	26
1	5	7	19	22
1	5	8	23	28
1	5	9	162	167
1	5	10	112	-116
1	5	11	35	34
1	5	12	36	36
1	5	13	-10	-4
1	5	14	-10	8
1	6	-13	45	44
1	6	-12	35	-29
1	6	-11	37	33
1	6	-10	41	43
1	6	-9	220	-229
1	6	-8	27	29
1	6	-7	48	-49
1	6	-6	42	44
1	6	-5	125	127
1	6	-4	75	-79
1	6	-3	61	58
1	6	-2	346	-354
1	6	-1	196	194
1	6	0	91	-90
1	6	1	66	-65
1	6	2	18	-16
1	6	3	34	36
1	6	4	9	-8
1	6	5	49	46
1	6	6	89	95
1	6	7	211	-219
1	6	8	-9	10
1	6	9	11	9
1	6	10	87	86
1	6	11	28	32
1	6	12	20	24
1	6	13	26	-27
1	7	-12	13	11
1	7	-11	31	-32
1	7	-10	12	-2
1	7	-9	81	-80
1	7	-8	15	14
1	7	-7	51	-53
1	7	-6	142	-144
1	7	-5	141	-55
1	7	-4	107	-113
1	7	-3	191	193
1	7	-2	259	-267
1	7	-1	131	131
1	7	0	100	-98
1	7	1	32	-36
1	7	2	351	360
1	7	3	110	103
1	7	4	227	244
1	7	5	35	25
1	7	6	120	124
1	7	7	23	-27
1	7	8	26	-28
1	7	9	85	-82
1	7	10	64	-68
1	7	11	121	-117
1	7	12	82	72
1	8	-10	94	91
1	8	-9	-10	5
1	8	-8	22	-24
1	8	-7	28	29
1	8	-6	-10	-2
1	8	-5	45	48
1	8	-4	70	78
1	8	-3	56	60
1	8	-2	69	73
1	8	-1	148	153
1	8	0	103	104
1	8	1	70	-69
1	8	2	92	-91
1	8	3	149	-156
1	8	4	122	-117
1	8	5	60	-66
1	8	6	-10	2
1	8	7	48	-49
1	8	8	35	-36
1	8	9	25	24
1	8	10	52	48
1	9	-7	34	-30
1	9	-6	21	17
1	9	-5	61	-59
1	9	-4	15	8
1	9	-3	40	35
1	9	-2	17	-17
1	9	-1	18	13
1	9	0	18	-19
1	9	1	20	-19
1	9	2	-10	3
1	9	3	37	36
1	9	4	37	-36
1	9	5	20	-19
1	9	6	-10	7
1	9	7	-10	-1
1	10	-1	19	19
1	10	0	23	23
1	10	1	30	-29
2	0	-16	15	15
2	0	-14	94	-89
2	0	-12	169	170
2	0	-10	19	12
2	0	-8	225	217
2	0	-6	56	46
2	0	-4	568	-572
2	0	-2	375	380
2	0	0	952	-1025
2	0	2	1210	-1263
2	0	4	315	323
2	0	6	252	250
2	0	8	509	502
2	0	10	-8	-1
2	0	12	139	-137
2	0	14	248	246
2	0	16	47	47
2	1	-17	25	-22
2	1	-16	56	56
2	1	-15	79	78
2	1	-14	-10	-5
2	1	-13	85	-89
2	1	-12	174	-184
2	1	-11	27	-31
2	1	-10	67	-63
2	1	-9	185	188
2	1	-8	10	11
2	1	-7	394	-366
2	1	-6	293	-279
2	1	-5	134	-127
2	1	-4	434	-435
2	1	-3	270	-279
2	1	-2	111	-121
2	1	-1	73	14
2	1	0	969	1004
2	1	1	1080	1262
2	1	2	922	996
2	1	3	25	20
2	1	4	78	-84
2	1	5	68	64
2	1	6	220	-226
2	1	7	29	24
2	1	8	12	11
2	1	9	265	-262
2	1	10	32	-30
2	1	11	72	68
2	1	12	63	-64
2	1	13	117	-116
2	1	14	18	-20
2	1	15	101	-103
2	1	16	30	28
2	2	-16	40	-43
2	2	-15	-10	-8
2	2	-14	12	15
2	2	-13	66	72
2	2	-12	179	184
2	2	-11	49	53
2	2	-10	157	-152
2	2	-9	73	-73
2	2	-8	15	-20
2	2	-7	161	155
2	2	-6	317	307
2	2	-5	52	41
2	2	-4	83	79
2	2	-3	278	-288
2	2	-2	350	353
2	2	-1	27	22
2	2	0	339	-342
2	2	1	86	-83
2	2	2	102	-101
2	2	3	60	-62
2	2	4	256	261
2	2	5	23	-29
2	2	6	312	-315
2	2	7	107	-115

Table 3. Continued.

H	K	L	F(O)	F(C)	H	K	L	F(O)	F(C)	H	K	L	F(O)	F(C)	H	K	L	F(O)	F(C)	H	K	L	F(O)	F(C)
2	2	8	41	43	2	6	-9	23	-16	3	1	-7	140	-144	3	4	3	25	23	3	8	8	-11	-2
2	2	9	39	37	2	6	-8	128	-132	3	1	-6	82	-76	3	4	4	11	-4	3	9	-6	21	-20
2	2	10	25	20	2	6	-7	-9	6	3	1	-5	64	-65	3	4	5	125	-128	3	9	-5	58	56
2	2	11	81	83	2	6	-6	158	-160	3	1	-4	144	-144	3	4	6	148	-143	3	9	-4	-11	-2
2	2	12	79	-82	2	6	-5	40	-44	3	1	-3	120	120	3	4	7	63	-63	3	9	-3	34	37
2	2	13	13	-14	2	6	-4	32	33	3	1	-2	123	-124	3	4	8	76	-79	3	9	-2	70	73
2	2	14	31	29	2	6	-3	130	-131	3	1	-1	83	84	3	4	9	138	-136	3	9	-1	14	13
2	2	15	14	-14	2	6	-2	72	74	3	1	0	98	-96	3	4	10	123	125	3	9	0	102	104
2	2	16	51	-48	2	6	-1	-9	1	3	1	1	128	134	3	4	11	48	-48	3	9	1	57	55
2	3	-16	-10	6	2	6	0	66	66	3	1	2	-7	3	3	4	12	148	148	3	9	2	43	-40
2	3	-15	-10	1	2	6	1	-8	2	3	1	3	178	186	3	4	13	156	155	3	9	3	31	-33
2	3	-14	42	36	2	6	2	16	-18	3	1	4	54	52	3	4	14	102	102	3	9	4	100	-101
2	3	-13	43	-43	2	6	3	31	-28	3	1	5	36	31	3	5	-14	78	-72	3	9	5	32	-33
2	3	-12	59	-64	2	6	4	41	-43	3	1	6	24	-27	3	5	-13	-10	4	4	0	-16	86	-85
2	3	-11	61	-54	2	6	5	23	-23	3	1	7	11	11	3	5	-12	10	-7	4	0	-14	25	25
2	3	-10	66	70	2	6	6	134	136	3	1	8	62	59	3	5	-11	65	-62	4	0	-12	21	20
2	3	-9	37	38	2	6	7	48	-47	3	1	9	-8	2	3	5	-10	66	62	4	0	-10	84	88
2	3	-8	-8	0	2	6	8	42	44	3	1	10	29	25	3	5	-9	129	139	4	0	-8	89	93
2	3	-7	121	-125	2	6	9	21	22	3	1	11	-9	1	3	5	-8	144	-154	4	0	-6	211	-220
2	3	-6	190	-180	2	6	10	58	-61	3	1	12	-9	5	3	5	-7	51	61	4	0	-4	275	273
2	3	-5	218	214	2	6	11	11	9	3	1	13	-10	5	3	5	-6	88	-91	4	0	-2	81	87
2	3	-4	162	161	2	6	12	13	-9	3	1	14	75	75	3	5	-5	115	-114	4	0	0	224	-216
2	3	-3	156	155	2	6	13	11	-7	3	1	15	-11	-1	3	5	-4	-8	0	4	0	2	179	171
2	3	-2	14	-15	2	7	-12	33	-37	3	1	16	-11	6	3	5	-3	33	-33	4	0	4	129	-138
2	3	-1	144	-153	2	7	-11	39	39	3	2	-16	-11	-6	3	5	-2	132	132	4	0	6	104	111
2	3	0	72	-74	2	7	-10	24	-30	3	2	-15	10	10	3	5	-1	87	-94	4	0	8	21	-17
2	3	1	22	-14	2	7	-9	-10	0	3	2	-14	-10	8	3	5	0	309	308	4	0	10	194	-195
2	3	2	177	172	2	7	-8	38	34	3	2	-13	75	82	3	5	1	26	26	4	0	12	96	93
2	3	3	405	-402	2	7	-7	15	8	3	2	-12	199	206	3	5	2	23	-28	4	0	14	44	-43
2	3	4	84	77	2	7	-6	39	-38	3	2	-11	123	-124	3	5	3	99	-99	4	1	-16	56	53
2	3	5	197	-192	2	7	-5	123	-124	3	2	-10	292	305	3	5	4	40	41	4	1	-15	32	-32
2	3	6	-7	5	2	7	-4	24	-24	3	2	-9	245	-247	3	5	5	55	-53	4	1	-14	28	-28
2	3	7	19	16	2	7	-3	132	-131	3	2	-8	-8	-16	3	5	6	113	118	4	1	-13	46	-42
2	3	8	114	-115	2	7	-2	78	78	3	2	-7	61	-56	3	5	7	203	209	4	1	-12	-10	11
2	3	9	75	74	2	7	-1	21	-17	3	2	-6	103	-102	3	5	8	50	-52	4	1	-11	130	130
2	3	10	190	-190	2	7	0	73	79	3	2	-5	198	188	3	5	9	88	86	4	1	-10	96	95
2	3	11	252	255	2	7	1	20	-18	3	2	-4	276	-264	3	5	10	13	11	4	1	-9	64	-63
2	3	12	31	-33	2	7	2	40	39	3	2	-3	363	349	3	5	11	20	-27	4	1	-8	78	78
2	3	13	62	65	2	7	3	63	67	3	2	-2	177	-171	3	5	12	63	-62	4	1	-7	65	63
2	3	14	30	27	2	7	4	79	-82	3	2	-1	58	57	3	5	13	72	-72	4	1	-6	59	61
2	3	15	21	-18	2	7	5	-10	-3	3	2	0	126	126	3	6	-13	39	40	4	1	-5	125	115
2	3	16	14	12	2	7	6	63	-63	3	2	1	49	48	3	6	-12	12	-11	4	1	-4	91	-98
2	4	-15	17	-20	2	7	7	16	-19	3	2	2	118	-121	3	6	-11	49	-48	4	1	-3	29	-25
2	4	-14	-10	-3	2	7	8	-10	4	3	2	3	151	157	3	6	-10	-10	-8	4	1	-2	88	-83
2	4	-13	10	14	2	7	9	109	110	3	2	4	56	61	3	6	-9	70	75	4	1	-1	255	269
2	4	-12	31	-35	2	7	10	20	22	3	2	5	70	67	3	6	-8	-10	0	4	1	0	105	-104
2	4	-11	36	33	2	7	11	-11	-4	3	2	6	88	89	3	6	-7	201	207	4	1	1	395	-407
2	4	-10	153	-152	2	8	-10	30	26	3	2	7	9	-13	3	6	-6	97	94	4	1	2	470	-480
2	4	-9	153	-154	2	8	-9	17	-19	3	2	8	19	19	3	6	-5	-9	4	4	1	3	349	-357
2	4	-8	126	-123	2	8	-8	15	-18	3	2	9	106	-103	3	6	-4	-9	10	4	1	4	244	-245
2	4	-7	78	-75	2	8	-7	14	-43	3	2	10	31	-31	3	6	-3	121	-124	4	1	5	130	132
2	4	-6	48	46	2	8	-6	32	-31	3	2	11	43	-40	3	6	-2	106	194	4	1	6	137	141
2	4	-5	41	-35	2	8	-5	58	53	3	2	12	46	-46	3	6	-1	532	-334	4	1	7	19	-16
2	4	-4	24	29	2	8	-4	21	27	3	2	13	14	-13	3	6	0	186	193	4	1	8	192	181
2	4	-3	85	78	2	8	-3	20	21	3	2	14	11	11	3	6	1	122	-120	4	1	9	159	162
2	4	-2	121	121	2	8	-2	29	-30	3	2	15	-10	-5	3	6	2	74	-78	4	1	10	62	62
2	4	-1	241	231	2	8	-1	11	-3	3	3	-16	66	65	3	6	3	183	186	4	1	11	-9	-5
2	4	0	73	65	2	8	0	22	18	3	3	-15	27	-23	3	6	4	117	-127	4	1	12	19	-13
2	4	1	192	-150	2	8	1	24	21	3	3	-14	29	-33	3	6	5	35	-24	4	1	13	57	-54
2	4	2	141	132	2	8	2	29	32	3	3	-13	19	20	3	6	6	151	-157	4	1	14	49	39
2	4	3	168	-158	2	8	3	78	74	3	3	-12	49	-54	3	6	7	46	51	4	1	15	111	111
2	4	4	132	124	2	8	4	26	-25	3	3	-11	168	-172	3	6	8	14	-18	4	2	-15	39	42
2	4	5	114	117	2	8	5	103	100	3	3	-10	46	50	3	6	9	85	87	4	2	-14	50	50
2	4	6	37	-34	2	8	6	40	37	3	3	-9	47	-54	3	6	10	18	22	4	2	-13	23	22
2	4	7	130	126	2	8	7	-10	-4	3	3	-8	22	-25	3	6	11	23	23	4	2	-12	120	-119
2	4	8	114	-122	2	8	8	-10	-5	3	3	-7	-8	3	3	6	12	67	-65	4	2	-11	106	-112
2	4	9	154	154	2	8	9	42	-41	3	3	-6	26	29	3	7	-11	-11	11	4	2	-10	118	-114
2	4	10	161	-161	2	9	-7	67	64	3	3	-5	8	1	3	7	-10	11	2	4	2	-9	93	92
2	4	11	69	68	2	9	-6	53	-48	3	3	-4	123	-111	3	7	-9	14	14	4	2	-8	88	83
2	4	12	-10	-4	2	9	-5	63	59	3	3	-3	289	278	3	7	-8	71	-74	4	2	-7	17	19
2	4	13	42	-40	2	9	-4	38	-31	3	3	-2	72	-61	3	7	-7	57	-59	4	2	-6	149	-147
2	4	14	78	72	2	9	-3	65	63	3	3	-1	45	-44	3	7	-6	66	69	4	2	-5	292	-288
2	4	15	34	-31	2	9	-2	24	24	3	3	0	221	219	3	7	-5	33	32	4	2	-4	109	-103
2	5	-14	50	-44	2	9	-1	69	68	3	3	1	-7	-16	3	7	-4	73	75	4	2	-3	161	-168
2	5	-13	48	-46	2	9	0	12	-7	3	3	2	138	-140	3	7	-3	10	12	4	2	-2	205	-206
2	5	-12	41	-37	2	9	1	25	-30	3	3	3	244	251	3	7	-2	43	-43	4	2	-1	75	-69
2	5	-11	48	-44	2	9	2	-10	5	3	3	4	162	-161	3	7	-1	130	-132	4	2	0	72	74
2	5	-10	77	75	2	9	3	34	-36	3	3	5	107	108	3	7	0	32	34	4	2	1	327	331
2	5	-9	188	186	2	9	4	17	-17	3	3	6	-11	-13	3	7	1	-9	4	4	2	2	535	536
2	5	-8	163	162	2	9	5	24	-22	3	3	7	14	-19	3	7	2	98	-96	4	2	3	425	424
2	5	-7	252	258	2	9	6	-11	-5	3	3	8	71	70	3	7	3	10	9	4	2	4	47	-45
2	5	-6	138	133	2	9	7	40	37	3	3	9	139	-139	3	7	4	76	-83	4	2	5	100	97
2	5	-5	33	34	3	0	-15	-9	10	3	3	10	92	96	3	7	5	-10	7	4	2	6	100	-100
2	5	-4	187	184	3	0	-13	-9	10	3	3	11	91	-91	3	7	6	26	-33	4	2	7	50	52
2	5	-3	119	-113	3	0	-11	49	-49	3	3	12	82	-83	3	7	7	-10	5	4	2	8	20	19
2	5	-2	119	-116	3	0	-9	67	75	3	3	13	58	-56	3	7	8	60	-60	4	2	9	59	-57
2	5	-1	103	-103	3	0	-7	214	216	3	3	14	71	-71	3	7	9	39	-39	4	2	10	16	15
2	5	0	279	-285	3	0	-5	54	-57	3	3	15	37	-38	3	7	10	54	55	4	2	11	161	-161
2	5	1	63	-67	3	0	-3	295	-309	3	4	-15	-11	-16	3	7	11	89	83	4	2	12	115	113
2	5	2	63	-57	3	0	-1	299	-314	3	4	-14	69	-66	3	8	-9	34	-30	4	2	13	101	-100
2	5	3	43	38	3	0	1	17	12	3	4	-13	36	33	3	8	-8	55	-51	4	2	14	27	-25
2	5	4	30	-28	3	0	3	31	-74	3	4	-12	29	-27	3	8	-7	11	10	4	2	15	38	-40
2	5	5	-8	1	3	0	5	-7	-9	3	4	-11	14	-16	3	8	-6	67	-62	4	3	-15	-11	11
2	5	6	47	52	3	0	7	27	29	3	4	-10	17	13	3	8	-5	36	-42	4	3	-14	57	-58
2	5	7	40	-36	3	0	9	40	41	3	4	-9	32	33	3	8	-4	95	-93	4	3	-13	26	29
2	5	8	27	25	3	0	11	120	123	3	4	-8	69	-70	3	8	-3	-10	-9	4	3	-12	87	91
2	5	9	30	28	3	0	13	40	-39	3	4	-7	18	-16	3	8	-2	-10	-12	4	3	-11	57	59
2	5	10	41	-43	3	0	15	122	-120	3	4	-6	192	194	3	8	-1	73	-73	4	3	-10	97	98
2	5	11	18	-19	3	1	-16	34	-33	3	4	-5	100	-101	3	8	0	73	-71	4	3	-9	103	-103
2	5	12	36	36	3	1	-15	62	59	3	4	-4	41	40	3	8	1	39	-41	4	3	-8	90	-92
2	5	13	31	-28	3	1	-14	40	-41	3	4	-3	181	189	3	8	2	27	28	4	3	-7	92	91
2	5	14	42	43	3	1	-13	75	71	3	4	-2	151	-144	3	8	3	120	118	4	3	-6	18	18
2	6	-13	60	57	3	1	-12	34	32	3	4	-1	64	63	3	8	4	207	208	4	3	-5	163	165
2	6	-12	54	49	3	1	-11	200	-206	3	4	0	27	-32	3	8	5	90	92	4	3	-4	47	46
2	6	-11	62	62	3	1	-10	179	183	3	4	1	69	-67	3	8	6	91	87	4	3	-3	85	-88
2	6	-10	69	62	3	1	-9	267	-272	3	4	2	81	-84	3	8	7	62	64	4	3	-2	33	-36
					3	1	-8	86	88																

Table 3. Continued.

H	K	L	F(O)	F(C)
4	3	-1	-7	-8
4	3	0	73	74
4	3	1	39	-39
4	3	2	194	-154
4	3	3	135	143
4	3	4	63	-63
4	3	5	141	140
4	3	6	15	-14
4	3	7	125	-128
4	3	8	-9	-1
4	3	9	85	-88
4	3	10	164	164
4	3	11	99	-96
4	3	12	83	81
4	3	13	55	-56
4	3	14	38	-38
4	4	-14	66	61
4	4	-13	-10	7
4	4	-12	18	-23
4	4	-11	44	-42
4	4	-10	16	-9
4	4	-9	28	32
4	4	-8	92	91
4	4	-7	38	-40
4	4	-6	33	-28
4	4	-5	23	-25
4	4	-4	36	-35
4	4	-3	224	221
4	4	-2	22	-21
4	4	-1	67	-66
4	4	0	20	8
4	4	1	107	-103
4	4	2	34	35
4	4	3	29	29
4	4	4	63	-64
4	4	5	80	-81
4	4	6	49	-50
4	4	7	33	-36
4	4	8	34	-34
4	4	9	65	-66
4	4	10	26	26
4	4	11	24	-24
4	4	12	49	46
4	4	13	73	73
4	4	14	18	-18
4	5	-13	48	-45
4	5	-12	31	27
4	5	-11	27	23
4	5	-10	52	-50
4	5	-9	52	-60
4	5	-8	154	-144
4	5	-7	198	-201
4	5	-6	24	25
4	5	-5	137	-134
4	5	-4	16	-14
4	5	-3	77	78
4	5	-2	56	-55
4	5	-1	175	175
4	5	0	95	90
4	5	1	54	52
4	5	2	11	9
4	5	3	23	-24
4	5	4	33	32
4	5	5	12	11
4	5	6	9	7
4	5	7	112	112
4	5	8	61	-61
4	5	9	40	38
4	5	10	13	14
4	5	11	37	-36
4	5	12	-11	10
4	5	13	-11	7
4	6	-12	-11	1
4	6	-11	113	-108
4	6	-10	14	14
4	6	-9	-10	-2
4	6	-8	90	94
4	6	-7	147	138
4	6	-6	163	165
4	6	-5	101	103
4	6	-4	69	69
4	6	-3	125	126
4	6	-2	96	-94
4	6	-1	39	37
4	6	0	152	-154
4	6	1	38	-37
4	6	2	114	-115
4	6	3	13	-14
4	6	4	37	39
4	6	5	40	-40
4	6	6	35	36
4	6	7	10	7
4	6	8	20	-19
4	6	9	20	-23
4	6	10	38	38
4	6	11	36	-37
4	7	-10	49	51
4	7	-9	32	30
4	7	-8	26	-23
4	7	-7	15	-17
4	7	-6	67	-67
4	7	-5	34	-36
4	7	-4	-10	-10
4	7	-3	17	19
4	7	-2	-9	-7
4	7	-1	-10	-2
4	7	0	-10	4
4	7	1	15	14
4	7	2	12	-17
4	7	3	25	-21
4	7	4	11	11
4	7	5	81	-80
4	7	6	59	60
4	7	7	21	20
4	7	8	19	22
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Table 3. Continued.

H	K	L	F(O)	F(C)	H	K	L	F(O)	F(C)	H	K	L	F(O)	F(C)	H	K	L	F(O)	F(C)	H	K	L	F(O)	F(C)
7	0	11	28	-27	7	3	-7	42	43	7	5	6	49	-49	8	2	-7	14	-12	8	5	-1	-10	10
7	1	-12	61	-61	7	3	-6	64	-65	7	5	7	58	55	8	2	-6	22	21	8	5	0	46	-43
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7	1	-9	40	-42	7	3	-3	99	-98	7	6	-6	44	-41	8	2	-3	12	9	8	5	3	21	21
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7	1	-7	19	-21	7	3	-1	-9	-8	7	6	-4	22	25	8	2	-1	68	66	9	0	-7	182	184
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7	1	-2	104	-102	7	3	4	33	30	7	6	1	33	-36	8	2	4	55	59	9	0	3	-10	7
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7	2	10	18	15	7	5	0	84	83	8	1	6	-10	-5	8	4	5	48	52	9	3	2	87	-84
7	2	11	67	-66	7	5	1	108	-106	8	1	7	46	43	8	4	6	30	33	9	3	3	70	66
7	3	-11	23	18	7	5	2	100	97	8	1	8	30	-25	8	5	-6	28	-26	9	3	4	38	-38
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7	3	-8	31	-34	7	5	5	74	72	8	2	-9	36	-31	8	5	-3	38	38	9	4	0	41	-43
										8	2	-8	27	26	8	5	-2	13	-11	9	4	1	50	49

observed and calculated U_{ij}'s are 0.0013 Å^2 and thus of the same order of magnitude as the e.s.d's of the thermal parameters obtained in the refinement. The libration tensor was used to calculate corrected bond lengths. The corrections are on the limit of significance being in most cases less than 3σ. A stereoscopic plot of the thermal ellipsoids at 50 % probability is shown in Fig. 1.
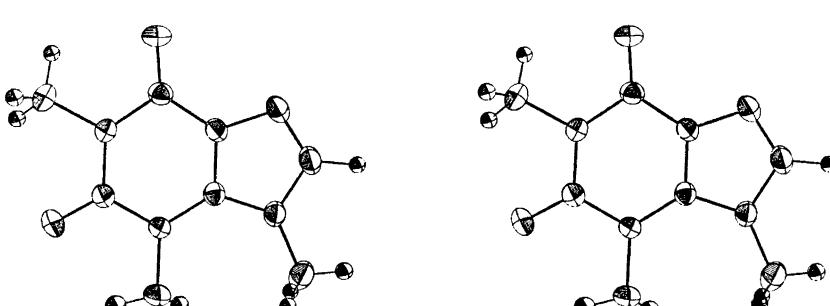
Fig. 1. The thermal ellipsoids plotted at the 50 % probability level. The isotropic thermal spheres of the hydrogen atoms are scaled down by a factor of four.
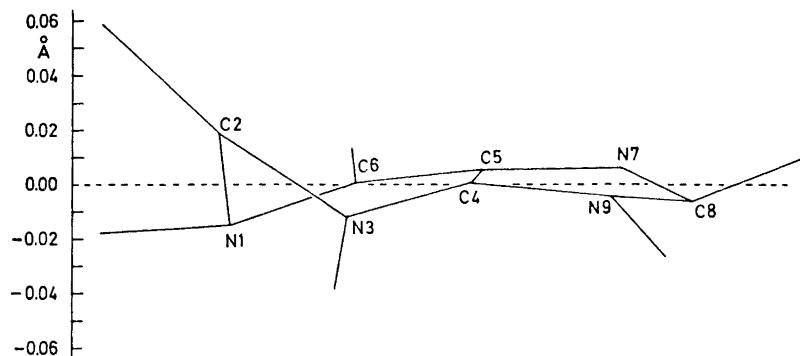
Fig. 2. The puckering of the molecule. The scale of the ordinate is greatly expanded relative to the abscissa.
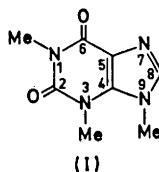
MOLECULAR STRUCTURE

The molecule is not planar, as shown in Fig. 2. The methyl groups on N(3) and N(9) are displaced to the same side of the purine ring. The imidazole ring is planar within experimental error. Five of the atoms in the pyrimidine ring are lying in one plane, while the sixth atom, C(2), deviates significanly from this plane. There is a small though probably significant dihedral angle of 0.7° between the planes through the two rings. The same feature is observed in several other purine derivatives.[8]

The molecular dimensions are shown in Fig. 3. The bond lengths C(4) − C(5) and N(7) − C(8) have a large degree of double bond character which is consistent with the most probable canonical form (I).

The small variation in the extra-anular C − N-bonds is probably significant and related to the strength of the adjacent bonds and to the magnitude of the internal angle at the substituted nitrogen atom. The difference in bond lengths

Fig. 3. Bond distances and angles. The estimated standard deviations are 0.002 Å and 0.1°, and 0.02 Å and 1° for non-hydrogen and hydrogen, respectively.

(I)
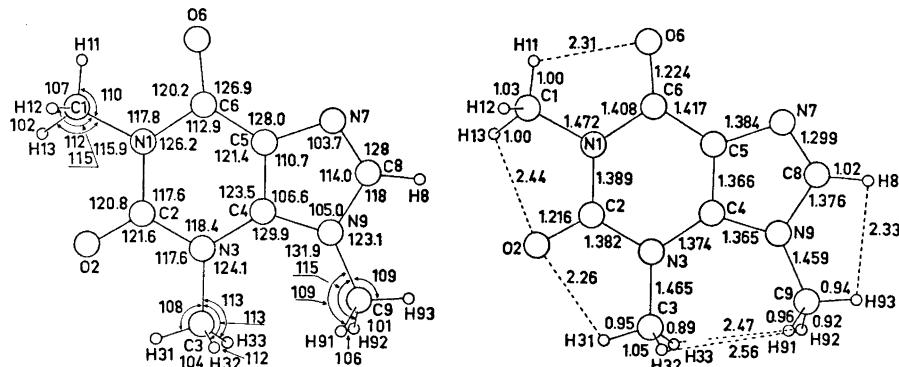
between the $C=O$ bond in 6-position and the one in 2-position is also significant. The $C(6)-O$ and $C(2)-O$ distances found in three analogous purine structures are in average 1.234 and 1.216 Å, respectively.[9-11]

The substituent on $C(6)$ in purines is always displaced so as to make the angle $C(5)-C(6)-X$ greater than 120°. For carbonyl groups the average of the external angle $C(5)-C(6)-O(6)$ is 127.8° (r.m.s. 0.3°) as calculated from 10 oxypurine structures.[8-15] In the present structure the angle is 126.9° and thus slightly reduced, probably because of the proximity of the methyl group on $N(1)$. The steric interaction between the methyl group on $N(3)$ and $N(9)$ has caused an increase in the angle $N(3)-C(4)-N(9)$ by approximately 2° compared to the average purine geometry.

MOLECULAR PACKING

A stereoscopic drawing of the crystal structure viewed along the a axis is shown in Fig. 4. There are no ordinary hydrogen bonds present in the structure, however, some of the $C-H\cdots O$ contacts between methyl and carbonyl groups may be classified as very week hydrogen bonds. In the stereo-diagram three bonds of this type are indicated: $C(9)-H(93)\cdots O(2)=3.35$ Å, $\angle CHO=157°$, $C(9)-H(92)\cdots O(6)=3.43$ Å, $\angle CHO=171°$, and $C(1)-H(12)\cdots O(2)=3.45$ Å, $\angle CHO \, 176°$.

The molecules related by unit translation along a are partially overlapping when viewed perpendicular to the purine plane (Fig. 5). The interplanar
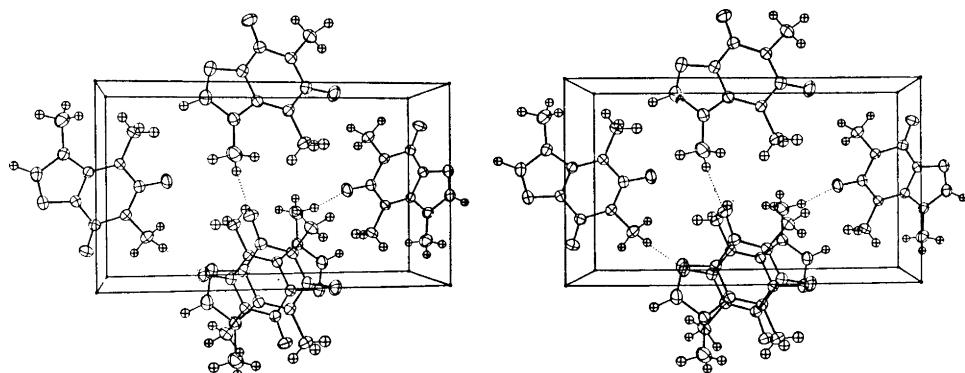
Fig. 4. Stereoscopic drawing of the packing of molecules in the unit cell. The a axis is nearly normal to the plane of the figure.
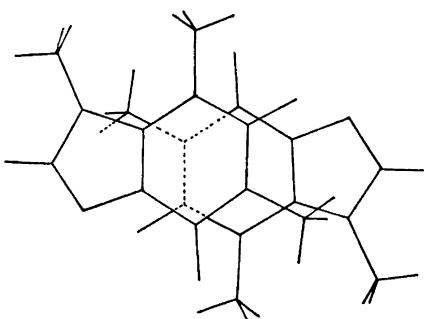
Fig. 5. Base stacking of TMX molecules viewed perpendicular to the least-squares plane of the purine ring. Interplanar spacing = 3.40 Å.

distance of 3.40 Å is slightly larger than what is normally found in stacks of simple purine-type molecules. The observed stacking pattern is not easily understood in terms of specific intermolecular forces. An excellent review on the subject of stacking interactions has recently been published.[8]

ELECTRONIC STRUCTURE

The usual CNDO/2 approximation and parameters were chosen to calculate charge distribution and dipole moment for the molecule. The theory of the CNDO/2 all valence electron calculation has been outlined by Pople *et al.*[16] The usefullness of this semiempirical method in predicting physical properties like dipole moment and rotation barriers seems to a certain degree to depend on the type of molecule and the atoms involved.

In Fig. 6 the calculated charge distribution and bond orders in TMX is given. The total dipole moment for the molecule is calculated to be 8.05 D. An experimental dipole moment is not yet determined due to solvation prob-

Fig. 6. Calculated charge distribution and bond orders obtained by the CNDO/2 method.
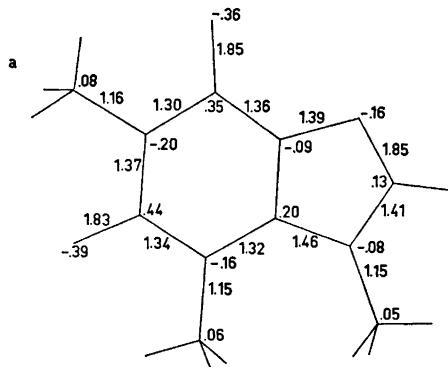
lems. However, in other xanthine molecules the dipole moments have been measured to be in the range $4.0 - 4.3$ D for $N(7) - H$ tautomers and $7.2 - 7.9$ D for $N(9) - H$ tautomers.[17] Introducing a methyl group instead of hydrogen on $N(9)$ should not alter the dipole moment significantly, thus the calculated value of 8.05 D seems reasonable.

CONFORMATION OF THE METHYL GROUPS

The main interest in this investigation concerns the orientation of the methyl groups in 3 and 9 position. Due to packing effects conformational studies on molecules in the solid state must be regarded with caution. In cases where several closely related structures are compared the conclusion about conformational aspects may be valid. In the present case the 1,3,9-trimethyl compound (TMX) is compared to 1,3-bis(8-theophyline)propane (BTP) [9] and to the 9-methyl hypoxanthine ligand (MHX) in a copper(II) complex [18] (Fig. 7).
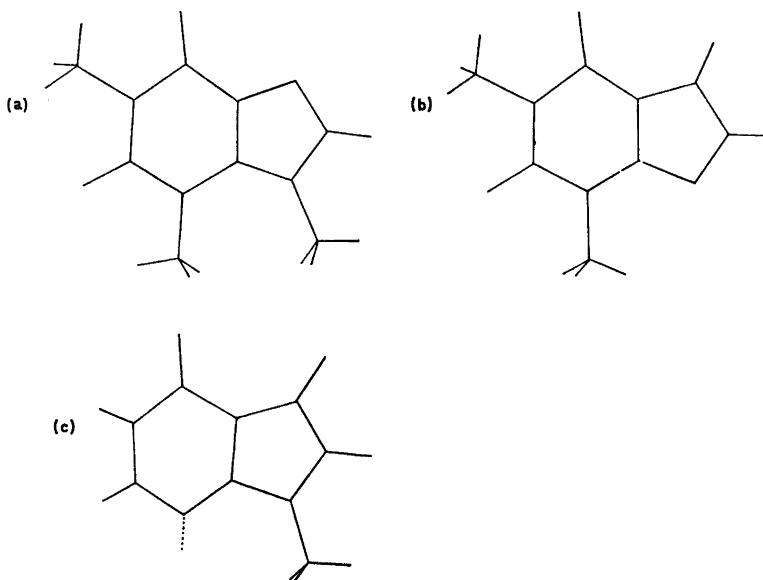
Fig. 7. Conformation of (a) 1,3,9-trimethyl-xanthine, (b) 1,3-bis(8-theophylline)propane, and (c) 9-methyl-hypoxanthine.

In the mono methyl substituted compound MHX the methyl group deviates 6° from an exactly eclipsed position relative to $C(8) - H(8)$. The $H(8)\cdots H(93)$ distance is only 2.3 Å. In TMX, Me(9) has exactly the same orientation within experimental error as in MHX despite the steric interference from Me(3). In BTP where the mutual methyl interaction is missing Me(3) is rotated 180° relative to the orientation in TMX. Thus the conformation with Me(3)

and Me(9) almost eclipsed seems to be more stable than the staggered conformation. In the observed eclipsed form the two shortest H$\cdots$H distances between the methyl groups are 2.47 and 2.56 Å, respectively, and thus not significantly different from the van der Waals contact of 2.50 Å. The O(2)$\cdots$H(31) distance on the other hand is only 2.26 Å compared to van der Waals distance O$\cdots$H of 2.6 Å. In a staggered configuration the O(2)$\cdots$Me(3) interaction is relieved somewhat, while the H(31)$\cdots$Me(9) contact becomes critical.

The molecular packing of TMX shows no short intermolecular contacts that might be expected to significantly alter the conformation of the molecule. The environment of the methyl group on N(1) is quite different in TMX and BTP; however, the orientations of the methyl groups in the two compounds are identical within experimental error. The O(6)$\cdots$H and O(2)$\cdots$H distances are 2.34 and 2.44 in TMX and 2.31 and 2.44 in BTP.

The above results are in agreement with NMR-spectra obtained by Bergmann and coworkers.[2] They report down field shifts of the 3- and 9-methyl signals of 0.17 p.p.m. relative to the compounds with only 3- or 9-substitution. This is interpreted as due to steric interference. *A priori* one would not expect the shifts to be of the same magnitude since Me(3) has changed its orientation completely while Me(9) has almost the same orientation as in the monosubstituted compound.

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