Acta Cryst. (1965). **19**, 573

The Crystal and Molecular Structure of Purine*

By David G. Watson†
Department of Biological Structure, University of Washington, Seattle, Washington, U.S.A.
and Robert M. Sweet and Richard E. Marsh
Gates and Crellin Laboratories of Chemistry, California, U.S.A.‡

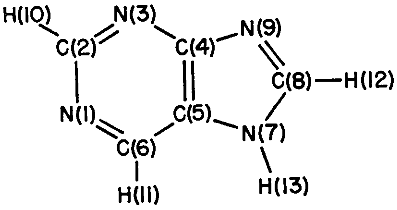
(*Received* 18 *December* 1964)

The crystal structure of purine, $C_5H_4N_4$, has been determined by X-ray diffraction techniques. Two entirely independent investigations were carried out. In each case complete three-dimensional intensity data were collected using Cu $K\alpha$ X-radiation and the structural parameters, including anisotropic temperature parameters for the heavy atoms, were refined by full-matrix least-squares techniques. The final R values for the two investigations are 0·048 and 0·070.

The unit cell is orthorhombic, space group $Pna2_1$, with $a=15{\cdot}55$, $b=9{\cdot}37$, and $c=3{\cdot}66$ Å; there are four molecules in the unit cell. The values of the bond distances found in the two investigations agree within experimental error (about 0·01 Å), and are in general agreement with values found in adenine derivatives. A proton is attached to atom N(7) of the five-membered ring rather than to N(9). The molecules are planar, and are joined together by relatively short (2·85 Å) N(7)–H · · · N(9) hydrogen bonds.

Introduction

This paper presents the results of two entirely independent investigations of the structure of purine (I).



(I)

The duplication of effort was discovered only when both three-dimensional studies were almost complete (Watson, 1964). Since different experimental techniques had been used, it was considered appropriate to publish both sets of results in the same paper and to make the necessary comparison between them. It has been a comfort to both parties that, except for systematic differences in the temperature factors, the two sets of results differ by less than their standard deviations.

In both laboratories the investigation was undertaken for essentially the same reasons. It was thought worthwhile to establish accurately the geometry of the purine ring system, which is the structural backbone of adenine and guanine, important components of the nucleic acids. Another interesting aspect of the study was the question of possible tautomerism of the atom H(13) between atoms N(7) and N(9).

For convenience, we shall divide the experimental portions of this paper into two parts, describing first the methods used by Watson (W) and then those used by Sweet and Marsh (SM).

Unit cell and intensity measurements

W

Considerable difficulty was experienced in attempting to recrystallize a commercial sample of purine. However, sublimation yielded a crop of rather poor crystals in the form of very thin plates elongated along *c*.

The crystal used for the determination of approximate unit-cell parameters and for the collection of intensity data had dimensions of the order of 0·03 × 0·3 × 1·5 mm. The final unit-cell parameters (Table 1) were measured with a Picker diffractometer using a smaller crystal.

Intensities on unidimensionally-integrated Weissenberg photographs were measured with a microdensitometer (Jensen, 1954) and recorded with a logarithmic slide-wire recorder. Within the linear response range of the film, the area under the recorder tracing is proportional to the integrated intensity. Data were collected for the layers *hk*0, *hk*1, *hk*2, and *hk*3 with Cu $K\alpha$ radiation. 327 reflections were of measurable intensity, corresponding to 44% of the total number of reflections within the Cu $K\alpha$ sphere. The usual Lorentz and polarization factors were applied but no corrections were made for absorption.

SM

Again, crystals were obtained only with difficulty, in this case by slow evaporation of methanol–water solu-

---

* This work was supported in part by a grant (AM-3288) from the National Institute of Arthritis and Metabolic Diseases, U.S. Public Health Service, and in part by a grant (G-21608) from the National Science Foundation, U.S.A.

† Present address: University Chemical Laboratories, Lensfield Road, Cambridge, England.

‡ Contribution No. 3197 from the Gates and Crellin Laboratories of Chemistry.

tions. They were considerably smaller than W's, about $0{\cdot}02\times0{\cdot}1\times1{\cdot}5$ mm. One crystal was mounted along the needle axis (c); a second was mounted along b and reduced to approximately square cross-section by rubbing with moist tissue paper.

Unit-cell dimensions were obtained from least-squares treatment of measurements on $hk0$ and $h0l$ Weissenberg photographs prepared with the film in the asymmetric position. Intensities were estimated visually from multiple-film equi-inclination Weissenberg photographs of layers 0–3 about c and 0–5 about b, taken with Cu $K\alpha$ radiation. After correction for Lorentz and polarization effects, they were correlated by means of a least-squares routine; since the spots on the b-axis photographs were somewhat misshapen, indicating a deformed crystal, their intensities were given half weight in the scaling procedure. Of a total of 730 reflections within the effective copper sphere, 640 were recorded, 570 being of measurable intensity. Most of the unrecorded reflections are of the type $hk4$ which, because of their general weakness and diffuseness (due to the deformed crystal), could not be measured on the b-axis photographs.

A statistical comparison of F^2 values for equivalent reflections measured from the two crystals indicated that the pattern of uncertainties F_o^2 (on an absolute scale) could be approximated by the expression

$$\sigma(F_o^2)=2{\cdot}44-0{\cdot}64F_o+0{\cdot}213F_o^2;$$

this expression was the basis of the weighting function used in the final least-squares refinements.

The crystal data are summarized in Table 1.

Table 1. *Crystal data*

Purine, $C_5N_4H_4$. M.W. 120·11. μ(Cu $K\alpha$), 9·8 cm^{-1}

	W	SM
a	$15{\cdot}553\pm3$ Å	$15{\cdot}551\pm2$ Å
b	$9{\cdot}374\pm1$	$9{\cdot}375\pm1$
c	$3{\cdot}664\pm1$	$3{\cdot}663\pm1$

(λ Cu $K\alpha=1{\cdot}5418$)

Systematic absences: $h0l$, $h=2n+1$; $0kl$, $(k+l)=2n+1$.
Space group, $Pna2_1$ or $Pnam$; $Pna2_1$ selected on the basis of packing considerations.
$Z=4$. $D_x=1{\cdot}493$ g.cm^{-3}; D_m(SM) $=1{\cdot}491$ g.cm^{-3}.

Determination and refinement of the structure

W

With such a very short c axis and four molecules per unit cell, it was decided to proceed on the assumption that the space group is $Pna2_1$. This space group has been confirmed by the solution and refinement of the structure. From packing considerations and a study of the strong reflections, a trial model was proposed for the centrosymmetric (001) projection. Structure factors calculated for this model gave $R=63\%$ and the corresponding Fourier synthesis showed that, although the six-membered ring was reasonably located, the manner of fusion of the five-membered ring was in error. Reassignment of the positions of atoms N(7) and C(8) resulted in a drop in R to 41% and the use of improved coordinates from a Fourier map further decreased R to 34%. Two cycles of isotropic least-squares refinement reduced R to 21%, at which stage the two-dimensional studies were terminated.

Since the 011 reflection was very intense, preliminary y coordinates were assigned assuming the molecule to be in this plane; atom C(6) was arbitrarily placed at $z=0$ to determine the origin. Structure factors corresponding to this model gave $R=35\%$ and the associated three-dimensional Fourier syntheses seemed very satisfactory. At this point the refinement process was initiated.

In the process of solution and refinement of the structure, the atomic scattering factors for nitrogen and carbon were those given by Berghuis, Haanappel, Potters, Loopstra, MacGillavry & Veenendaal (1955), and for hydrogen those of McWeeny (1951). The structure was refined by least-squares analysis based on the observed reflections only; at an intermediate stage, a three-dimensional difference synthesis was computed to determine the positions of the hydrogen atoms.

The least-squares program used in these calculations was the Busing, Martin & Levy (1962) full-matrix FORTRAN program adapted for our IBM 709 crystallographic system by Dr James M. Stewart. The function minimized was $\Sigma w(F_o-F_c)^2$, and the weighting scheme was that suggested by Hughes (1941). Seven

Table 2. *Synopsis of three-dimensional refinement of purine* (W)

In this table X, Y, Z and x, y, z denote coordinates of heavy atoms and hydrogen atoms, respectively. K_{1-4} denotes the four separate level scale factors and K is the composite scale factor.

Calculation	Refining or determining	Discrepancy index R(%)	$\Sigma w(\Delta F)^2$	Remarks
Structure factors and 3-D F_o map		35·4		X, Y, B from 2-D refinement. Trial Z coordinates.
LS cycles 1–4	X, Y, Z, B, K_{1-4}	33·8–16·0	3526–1542	
LS cycles 5–6	X, Y, Z, β_{ij}	16·5–9·1	669–135	Anisotropic thermal refinement commenced. No refinement of scale.
3-D diff. map	x, y, z			Hydrogen peaks of 0·27–0·33 e.Å^{-3}.
LS cycles 7–9	x, y, z	7·0–7·0	99–96	
LS cycles 10–11	X, Y, Z, β_{ij}	7·0–5·5	96–63	
LS cycles 12–13	x, y, z, K	5·0–4·9	49–47	Single scale K applied and data edited.
LS cycles 14–15	X, Y, Z, β_{ij}, K	4·9–4·8	47–44	

low-order reflections for which $|F_o|$ was less than $|F_c|$ were given zero weight since they were considered to be affected by extinction. A summary of the refinement procedure is presented in Table 2.

At the outset an attempt was made to refine the four individual level scale factors but a singular matrix resulted. Thus for the first eleven cycles the individual scale factors were adjusted between each cycle but not refined in the least-squares process. After least-squares cycle 11 the data were placed on a common scale and this single scale factor was then refined.

The peaks corresponding to hydrogen atoms in the three-dimensional difference synthesis were reasonably well defined except for the hydrogen attached to N(7). Since there is a possibility of tautomerism of the hydrogen between N(7) and N(9), particular attention was given to this problem. Two least-squares cycles, not quoted in Table 2, were computed in which a half-hydrogen was assigned to each of N(7) and N(9). Refinement of H(10), H(11), H(12) and the two half-hydrogens resulted in the half-hydrogen attached to N(9) shifting to a position about 1 Å from N(7) of the neighbouring hydrogen-bonded molecule. On this basis it seemed fairly certain that the hydrogen was indeed located on N(7). However, the final 3-D difference map indicates that the electron density distribution of H(13) is much more smeared than those for the other hydrogen atoms. In these calculations each hydrogen atom was assigned an isotropic B value of 3·0 Å^2 but no refinement of the thermal parameters was attempted.

The final R index, from which the extinguished reflections and the unobserved reflections were excluded, was 4·8%. The maximum coordinate shift in least-squares cycle 15 was 0·45 of its standard deviation and the maximum temperature parameter shift was 1·10 σ.

SM

A trial structure was derived on the basis of packing considerations and with the assumption that a hydrogen bond would be formed between atoms N(7) and N(9) of adjacent molecules (whichever of these atoms is protonated, the other has increased electronegativity and hence becomes a good hydrogen-bond acceptor). Structure factors calculated by hand for 15 low-order *hk*0 reflections showed satisfactory agreement with the observed values; these 15 reflections were included in an electron-density projection which led to improved x and y coordinates. Two-dimensional least-squares refinement, during which individual anisotropic temperature factors were introduced, led to an R value of 0·10; a difference map calculated towards the end of the refinement clearly showed the positions of the hydrogen atoms and in particular H(13), which lay near N(7) rather than N(9).

Three-dimensional least-squares refinement was carried out on an IBM 7094 computer under the CRYRM crystallographic system (Duchamp, 1964). The form factors were from *International Tables for X-ray Crystallography* (1962), and the quantity minimized was $\Sigma w(F_o^2 - KF_c^2)^2$. Various weighting functions were used, depending on the stage of refinement; during the last few cycles, when it appeared that the discrepancies between F_o^2 and KF_c^2 lay within the observational uncertainties, weights were taken equal to the inverses of the squares of the standard deviations in F_o^2 (see *Intensity measurements*). Unobserved reflections were included only if the values of KF_c^2 exceeded the threshold value of F_o^2. The full matrix of the normal equations was collected and inverted. Since the c axis is polar, the matrix is in principle singular; however, round-off effects were apparently large enough to remove the

Table 3. *The final heavy-atom coordinates and their estimated standard deviations*

All values have been multiplied by 10^4. The temperature factor is of the form
$\exp\{-(\beta_{11}h^2+\beta_{22}k^2+\beta_{33}l^2+2\beta_{12}hk+2\beta_{13}hl+2\beta_{23}kl)\}$

		x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
N(1)	W	30(4)	3047(6)	1274(30)	35(3)	81(6)	562(70)	6(4)	12(9)	−15(21)
	SM	37(3)	3041(4)	1257(*)	61(2)	128(4)	1057(46)	0(2)	−2(8)	6(15)
C(2)	W	154(6)	1693(7)	2402(31)	40(4)	81(8)	530(82)	−13(5)	−7(12)	−10(19)
	SM	160(3)	1689(5)	2390(*)	58(2)	133(6)	1172(69)	−12(3)	8(9)	21(16)
N(3)	W	888(4)	947(5)	2406(25)	41(3)	49(5)	398(53)	−12(4)	8(10)	17(13)
	SM	889(3)	960(4)	2462(*)	66(2)	103(4)	840(36)	−13(2)	6(7)	44(11)
C(4)	W	1561(4)	1701(7)	1205(34)	28(4)	51(6)	389(56)	1(3)	−18(11)	22(16)
	SM	1561(3)	1700(4)	1223(*)	60(2)	80(4)	825(40)	−1(2)	−11(8)	36(11)
C(5)	W	1505(4)	3117(7)	−46(29)	34(3)	44(6)	278(61)	−5(4)	−12(10)	28(15)
	SM	1501(3)	3103(4)	−41(*)	59(2)	82(4)	733(42)	−2(2)	−24(8)	25(11)
C(6)	W	701(5)	3772(7)	0(*)	38(4)	58(7)	566(73)	11(4)	−8(12)	33(17)
	SM	704(2)	3761(4)	13(*)	68(2)	97(4)	1065(56)	11(3)	−23(10)	31(13)
N(7)	W	2325(4)	3467(5)	−1105(27)	29(3)	57(6)	636(63)	−10(4)	−11(11)	20(16)
	SM	2316(3)	3465(5)	−1151(*)	60(2)	99(4)	921(42)	−10(2)	−9(8)	78(11)
C(8)	W	2809(5)	2330(8)	− 447(37)	24(3)	124(10)	531(61)	2(5)	−16(12)	−14(24)
	SM	2812(2)	2332(4)	−465(*)	54(2)	132(5)	896(45)	−1(3)	1(10)	17(15)
N(9)	W	2399(4)	1232(5)	927(28)	36(3)	48(5)	566(60)	6(4)	−17(11)	11(14)
	SM	2396(3)	1241(5)	929(*)	59(2)	106(4)	946(40)	8(2)	−15(8)	53(11)

* In W, the z coordinate of C(6) was constrained to the value 0 and was omitted from the refinement. In SM, all coordinates were included in the full-matrix refinement and no meaningful standard deviations in the z coordinates are available. The z coordinates of SM have been incremented so that the average values of z are the same for both determinations.

singularity and in no refinement cycle did the program fail to win a satisfactory inverse. Accordingly, the z coordinates refined satisfactorily; however, their standard deviations are without meaning.

The positional coordinates of all 13 atoms and the anisotropic temperature parameters of the 9 heavy atoms were adjusted; the temperature factors of the hydrogen atom were assumed to be isotropic, with $B = 3{\cdot}5$ Å^2. In the last refinement cycle the largest shift in any heavy-atom parameter was 12% of its standard deviation and in a hydrogen-atom coordinate, 35%. The final R value for 568 observed reflections of non-zero weight is 0·070. The 'goodness of fit' – $\Sigma w(F_o^2 - F_c^2)^2/(n-p)$ – is 0·76. That this value is less than unity suggests that, in general, the observational errors are smaller than the values reflected by the weighting function.

At the conclusions of the refinement, an electron density map and a difference map were calculated in the plane of the purine molecule. These maps are shown in Fig. 1.

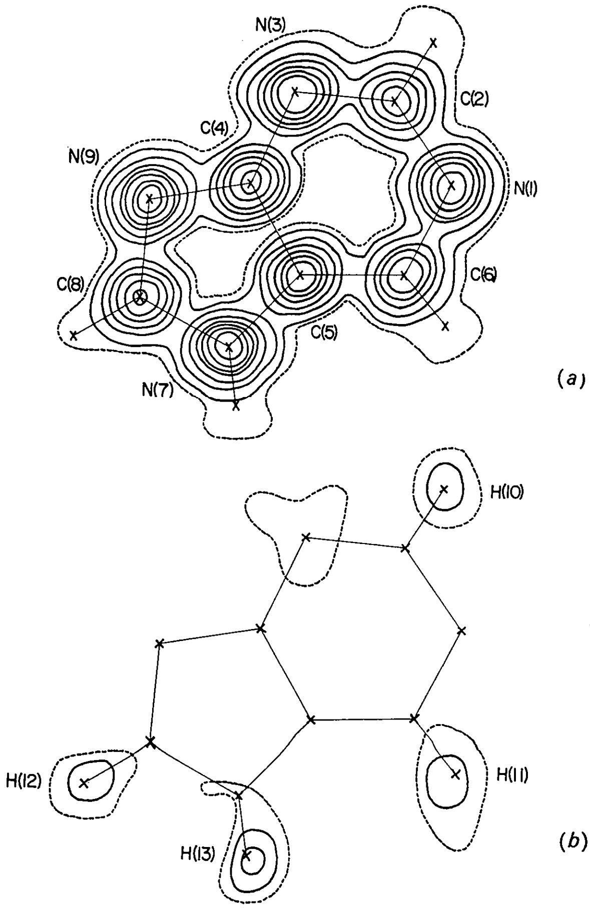


Fig. 1. (a) The electron density in the plane of the purine molecule, calculated at the conclusion of the refinement (SM). Contours are at intervals of 1 e.Å^{-3} beginning at 1 e.Å^{-3} (dashed). (b) The final difference map (SM) in the plane of the molecule; the contributions of the hydrogen atoms were omitted from the F_{cal}'s. Contours are at 0·1 e.Å^{-3} beginning with 0·1 e.Å^{-3} (dashed).

Table 4. *Final hydrogen coordinates and their standard deviations*

Atom		x	y	z
H(10)	W	−0·033(4)	0·112(8)	0·383(24)
	SM	−0·034(3)	0·125(5)	0·352
H(11)	W	0·061(4)	0·476(7)	−0·096(22)
	SM	0·056(3)	0·464(5)	−0·104
H(12)	W	0·342(5)	0·233(8)	−0·068(19)
	SM	0·346(4)	0·232(4)	−0·130
H(13)	W	0·241(4)	0·430(7)	−0·219(26)
	SM	0·246(3)	0·420(5)	−0·229

The final heavy-atom parameters, and their standard deviations, for the two structure determinations are given in Table 3. Coordinates of the hydrogen atoms are given in Table 4, and the observed and calculated structure factors in Table 5.

Molecular dimensions

The bond distances and angles for the two determinations, calculated from the parameters in Tables 3 and 4, are shown in Fig. 2. The estimated standard deviations in the distances and angles involving the heavy atoms are about 0·01 Å and 0·8° (W) and 0·006 Å and 0·5° (SM), the differences between the two sets of standard deviations being a reflection of the larger number of intensities observed by SM (570 *vs.* 327); the uncertainties in values involving hydrogen atoms

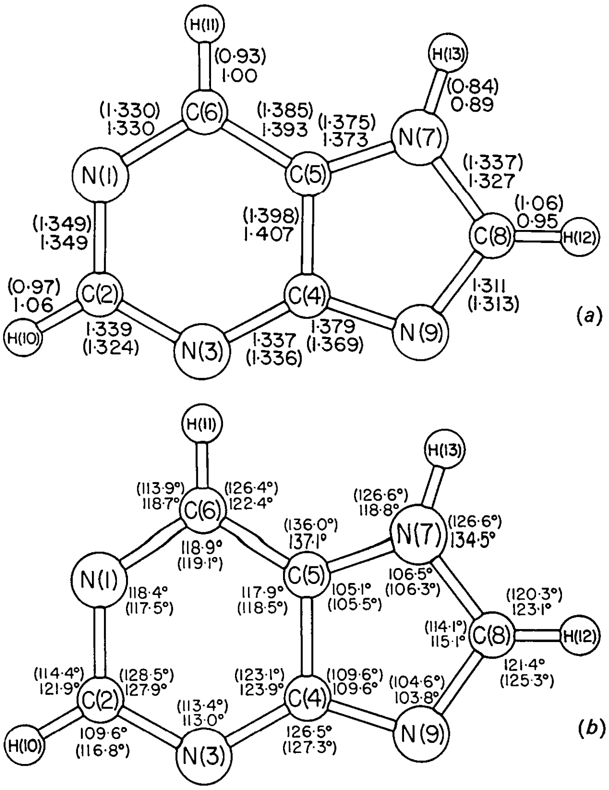


Fig. 2. The bond distances (*a*) and angles (*b*) calculated from the final coordinates. The values in parentheses are those of SM; the others, W.

Table 5. *Observed and calculated structure factors*

Reading from left to right, the columns contain values of k, $10F_o$ (SM), $10|F_c|$ (SM), α(SM), $10F_o$ (W), $10|F_c|$ (W), and α(W). A negative sign preceding $10F_o$ should be read 'less than'; an asterisk signifies that the reflection was given zero weight in the final least-squares cycles.

k	10Fo (SM)	10|Fc| (SM)	α(SM)	10Fo (W)	10|Fc| (W)	α(W)
0,k,0						
0	---	2480	0	---	2480	0
2	525*	694	180	575*	681	180
4	352*	452	180	428*	488	180
6	136	147	0	166	170	0
8	-11	7	180			
10	20	20	0			
12	9	8	0			
1,k,0						
1	56	51	0	49	50	0
2	102	98	180	96	100	180
3	64	60	0	64	65	0
4	95	84	180	90	98	180
5	149	145	180	161	161	180
6	34	35	0			
7	31	32	0			
8	57	59	0	90	84	0
9	37	40	180			
10	23	22	180	43	37	180
11	28	28	0	52	45	0
12	-4	0	0			
2,k,0						
0	124	127	180	132	133	180
1	498*	587	180	524*	593	180
2	91	97	0	88	102	0
3	262	269	180	266*	286	180
4	32	33	0	38	39	0
5	194	193	0	215	213	0
6	-9	2	0			
7	42	39	180			
8	62	67	180	88	97	180
9	38	44	0			
10	52	52	0	81	80	0
11	11	11	180			
12	4*	7	180			
3,k,0						
1	35	31	180	33	29	180
2	-5	8	180			
3	23	22	180			
4	29	28	180	31	31	180
5	27	29	0			
6	22	20	180			
7	-10	1	0			
8	37	34	180			
9	-10	4	180			
10	66	75	0	106	118	0
11	-7	5	180			
4,k,0						
0	442	490	0	490	511	0
1	87	92	180	99	96	180
2	206*	235	180	234	254	180
3	88	89	180	91	98	180
4	79	75	180	86	83	180
5	107	102	180	124	112	180
6	72	69	0	85	89	0
7	118	124	0	161	157	0
8	49	51	0	63	66	0
9	15	17	180			
10	46	39	180	63	56	180
11	22	20	180			
5,k,0						
1	80	79	180	89	86	180
2	19	22	0			
3	54	56	0	62	61	0
4	19	19	180			
5	45	42	180	48	47	180
6	32	32	180			
7	93	86	0	115	116	0
8	74	75	0	108	102	0
9	25	25	180			
10	17	19	180			
11	-7	7	180			
6,k,0						
0	109	103	180	126	116	180
1	16	1	180			
2	238	257	180	293	292	180
3	138	148	180	167	167	180
4	222	217	0	257	252	0
5	117	123	0	150	149	0
6	156	154	0	197	204	0
7	-10	2	0			
8	135	156	180	218	225	180
9	41	41	180			
10	12	17	0			
11	-6	1	180			
7,k,0						
1	28	27	0	37	39	0
2	45	47	0	55	54	0
3	53	58	180	67	71	180
4	102	105	0	130	129	0
5	-9	3	180			
6	29	30	180			
7	86	91	0	135	127	0
8	66	71	180	111	111	180
9	33	34	180			
10	31	34	0	57	57	0
11	35	33	180			
8,k,0						
0	222	241	0	291	280	0
1	92	87	180	116	114	180
2	130	143	180	169	170	180
3	233	233	0	293	287	0
4	30	28	180	45	43	180
5	24	19	180			
6	75	77	0	107	115	0
7	109	105	180	156	158	180
8	44	44	180	68	66	180
9	26	25	0			
10	-8	1	0			
11	17	16	0			
9,k,0						
1	21	19	0			
2	18	18	180			
3	68	65	0	86	84	0
4	19	17	0			
5	85	90	180	131	124	180
6	54	55	0	85	78	0
7	-11	8	0			
8	37	36	180	50	47	180
9	20	22	0			
10	19	20	180			
10,k,0						
0	56	53	180	83	75	180
1	13	1	180			
2	13	8	0			
3	-10	12	180			
4	61	63	0	92	96	0
5	66	67	0	97	103	0
6	58	65	180	94	102	180
7	48	52	180	78	83	180
8	-10	6	180			
9	12	6	180			
10	16	17	0			
11,k,0						
1	41	41	0	58	59	0
2	24	25	180			
3	34	29	180			
4	24	27	0			
5	-11	0	0			
6	23	22	180			
7	-10	3	180			
8	-9	4	0			
9	15	11	180			
10	-4	1	0			
12,k,0						
0	148	152	0	236	230	0
1	53	52	0	81	84	0
2	34	27	180			
3	47	45	0	73	73	0
4	76	78	180	117	122	180
5	67	74	180	114	124	180
6	27	31	0			
7	14	15	0			
8	17	16	180			
9	13	10	0			
13,k,0						
1	15	11	180			
2	69	74	180	117	107	180
3	40	41	0	67	65	0
4	15	2	0			
5	38	41	180	66	68	180
6	30	33	0	49	60	0
7	13	11	0			
8	10	11	180			
9	-5	1	180			
14,k,0						
0	80	82	0	138	142	0
1	89	92	180	158	152	180
2	60	60	180	100	100	180
3	36	38	180	67	67	180
4	15	14	0			
5	56	58	0	100	108	0
6	13	10	0			
7	18	19	180			
8	10	9	180			
15,k,0						
1	31	31	180	44	51	180
2	15	12	180			
3	27	23	0			
4	14	3	0			
5	13	12	0			
6	-8	5	180			
7	-7	3	0			
8	-3	0	180			
16,k,0						
0	30	29	180			
1	14	12	180			
2	16	16	0			
3	13	7	0			
4	-9	6	180			
5	-8	1	180			
6	-7	4	0			
7	8	6	180			
17,k,0						
1	16	14	180			
2	-9	1	180			
3	18	14	0			
4	-8	3	0			
5	-7	0	0			
6	-5	7	0			
18,k,0						
0	13	11	0			
1	17	17	180			
2	21	18	180			
3	3	6	180			
4	15	15	0			
5	11	12	0			
19,k,0						
1	-6	5	180			
2	10	7	0			
3	-5	5	0			
0,k,1						
1	480*	965	113	849*	1039	113
3	163	151	182	157	159	181
5	201	205	300	233	243	297
7	26	26	107	33	36	107
9	52	52	13	84	83	7
11	19	19	141	26	40	130
1,k,1						
1	211*	296	181	273*	313	181
2	319	344	221	315*	364	221
3	247	233	8	224	245	9
4	117	109	105	114	121	107
5	67	67	325	81	86	321
6	66	64	342	75	77	344
7	55	56	197	67	66	197
8	28	29	113			
9	43	37	52	60	55	68
10	37	32	315	45	49	326
11	20	18	228			
2,k,1						
0	328*	482	129	502	518	128
1	323*	424	215	408	451	216
2	89	80	290	77	80	287
3	41	40	351	37	41	350
4	188	173	301	193	203	301
5	70	70	48	87	79	51
6	93	98	76	124	119	75
7	51	54	152	68	75	157
8	32	32	292	38	41	297
9	48	47	306	89	72	310
10	25	23	141	40	39	141
11	26	23	60	37	37	51
3,k,1						
1	143	145	257	160	152	256
2	135	122	330	123	130	327
3	106	105	127	109	107	127
4	79	75	182	86	76	182
5	60	63	57	70	79	60
6	45	44	40	55	53	43
7	60	63	6	84	85	2
8	23	21	232			
9	77	69	255	107	101	258
10	-9	6	144			
11	31	30	145	53	60	153
4,k,1						
0	113	94	166	118	111	162
1	183	194	107	206	210	108
2	55	50	157	62	59	154
3	95	83	11	99	94	7
4	101	87	26	103	97	23
5	38	37	324	45	49	324
6	87	90	287	117	115	289
7	58	57	247	74	74	240
8	57	60	92	90	83	89
9	45	44	92	61	61	88
10	13	15	197			
11	24	21	179	42	40	169
5,k,1						
1	136	129	193	144	142	193
2	20	19	290			
3	83	74	13	81	80	16
4	134	123	47	147	143	48
5	63	63	22	79	81	16
6	75	77	282	102	98	286
7	63	71	240	96	94	238
8	62	64	170	101	97	173
9	38	34	103	54	53	108
10	10	6	80			
11	18	13	41	27	25	39
6,k,1						
0	8	11	29			
1	152	142	180	164	168	181
2	109	105	72	130	125	69
3	214	209	312	263	257	312
4	135	125	260	157	148	260
5	78	77	22	102	103	22
6	24	19	70			
7	153	161	137	224	231	137
8	40	38	106	55	56	102
9	71	70	273	118	112	271
10	9	11	251			
11	26	26	352	47	49	346
7,k,1						
1	112	92	346	117	109	347
2	107	101	28	121	116	29
3	25	22	188			
4	40	35	42	55	50	35
5	83	77	166	107	102	162
6	71	69	256	91	91	255
7	18	14	93			
8	56	46	143	77	73	148
9	43	37	309	67	66	306
10	35	31	48			
11	3*	7	116			
8,k,1						
0	77	79	104	102	99	105
1	133	130	126	173	161	127
2	144	136	304	178	169	302
3	43	38	321	56	49	324
4	101	88	88	112	113	86
5	39	37	301	48	54	300
6	100	105	171	152	154	168
7	39	38	130	60	58	126
8	59	54	303	94	90	300
9	18	15	303			
10	32	30	18	56	58	18
9,k,1						
1	39	40	108	56	50	108
2	52	47	200	66	61	206
3	69	68	353	84	93	356
4	76	66	110	98	97	112
5	88	81	235	120	114	235
6	57	52	314	74	80	314
7	51	51	136	75	78	144
8	13	10	252			
9	36	35	34	66	67	43
10	13	12	116	42	30	105
10,k,1						
0	20	18	284			
1	82	80	233	116	112	237
2	40	36	45	48	52	45
3	41	40	260	55	57	258
4	45	45	236	68	63	237
5	67	65	102	92	101	98
6	32	29	107	51	50	113
7	22	21	255			
8	11	8	281			
9	28	25	352	54	49	348
11,k,1						
1	29	26	21			
2	21	18	17			
3	28	28	209			
4	55	54	203	70	82	203
5	14	13	98			
6	14	15	56			
7	13	12	293			
8	24	21	32	47	42	34
9	15	10	73			
12,k,1						
0	86	89	249	127	139	249
1	88	86	141	139	139	140
2	12	8	71			
3	30	29	115			
4	64	70	77	114	117	78
5	45	47	287	84	76	284
6	44	43	250	75	77	253
7	20	15	87			
8	10	12	7			
9	14	13	326			
13,k,1						
1	43	45	150	59	69	148
2	61	60	214	102	104	216
3	39	40	333	71	59	331
4	39	38	73	63	66	75
5	20	18	296	49	37	299
6	28	26	319	53	50	323
7	19	19	95			
8	13	11	150			
14,k,1						
0	73	75	136	130	129	133
1	57	60	101	108	105	103
2	20	16	299			
3	26	25	289			
4	40	38	301	67	73	299
5	-9	6	359			
6	26	25	88	56	54	90
7	16	15	160			
8	9	8	297			
15,k,1						
1	24	21	209			
2	49	46	330	85	85	330
3	24	25	30	38	40	27
4	14	15	163			
5	10	5	63			
6	9	7	125			
7	7	6	219			
16,k,1						
0	29	25	185	53	52	186
1	17	16	255			
2	13	12	339			
3	30	26	49	62	55	53
4	20	12	48			
5	9	8	254			
6	13	12	187			
17,k,1						
1	-8	4	248			
2	10	7	348			
3	-8	7	56			
4	-7	4	97			
5	-6	4	261			
18,k,1						
0	13	12	85			
1	16	14	73			
2	-7	2	42			
3	14	13	307			
4	11	10	273			
19,k,1						
1	6	5	291			
2	9	10	351			
3	1*	4	29			
0,k,2						
0	123	137	49			
2	102	109	196	133	140	199
4	66	61	295	82	80	290
6	39	35	68	54	51	56
8	42	44	320	59	60	319
10	25	25	100			
1,k,2						
1	113*	164	176	187	203	175
2	199	221	290	261	268	291
3	146	141	5	172	179	4
4	78	72	104	93	89	106
5	33	32	314	46	47	310
6	64	63	95	91	85	93
7	26	26	89	43	40	93
8	61	56	271	57	71	272
9	20	21	239			
10	22	20	143			
2,k,2						
0	153*	215	149	262	271	151
1	68	81	249	102	100	251
2	134	144	305	167	182	310
3	36	38	18	43	44	7
4	59	54	77	66	69	79
5	61	54	18	81	79	19
6	26	24	87	36	37	107
7	43	43	203	62	64	199
8	31	31	275	75	60	290
9	-7	8	113			
10	-6	4	225			
3,k,2						
1	74	90	266	110	110	266
2	209	229	31	259	276	29
3	158	153	91	185	187	91
4	29	30	290	41	41	308
5	75	77	297	102	101	297
6	71	74	242	108	103	235
7	40	41	175	66	60	174
8	50	49	147	75	77	150
9	20	17	55			
10	19	16	42			
4,k,2						
0	12	11	88			
1	43	45	60	63	57	54
2	48	45	2	64	61	358
3	46	45	331	56	56	326
4	11	5	191			
5	24	18	168			
6	81	86	199	120	120	197
7	29	25	7	42	44	8
8	54	50	13			
9	37	36	177			
10	29	30	95			
5,k,2						
1	62	61	21	78	73	13
2	69	68	283	86	86	289
3	32	26	306	37	32	333
4	52	47	333	63	64	329
5	91	87	199	128	131	198
6	72	82	138	115	118	135
7	33	34	96	54	53	103
8	16	20	325			
9	25	22	354			
10	24	24	303			
6,k,2						
0	115	114	96	154	146	89
1	55	58	359	80	76	356
2	94	92	284	126	126	285
3	88	77	171	108	99	168
4	29	19	22	42	31	32
5	40	36	290	54	49	285
6	69	70	105	102	110	108
7	43	43	52	66	63	45
8	57	56	226			
9	-6	9	172			
10	22	25	337			
7,k,2						
1	59	55	307	77	75	308
2	62	54	73	79	77	75
3	48	50	70	71	69	69
4	47	46	181	70	63	179
5	76	76	187	115	111	184
6	35	34	288	53	55	280
7	-8	12	32			
8	16	16	19			
9	42	40	337			
10	9	12	86			
8,k,2						
0	65	62	107	91	87	110
1	71	71	214	102	93	215
2	30	25	285			
3	22	22	340			
4	10	11	328			
5	71	69	122	107	103	123
6	12	14	166			
7	44	42	279	78	78	279
8	-7	0	258			
9	22	24	353			
9,k,2						
1	19	11	82			
2	69	67	245	106	99	245
3	-8	6	139			
4	73	71	158	114	112	157
5	44	43	264	71	74	259
6	51	52	25	77	82	24
7	24	24	68			
8	28	29	324			
9	14	12	77			
10,k,2						
0	79	79	183	133	133	183
1	43	41	354	71	69	358
2	20	15	318			
3	30	31	162	45	47	159
4	49	47	34	75	73	31
5	25	23	255	40	37	251
6	16	13	185			
7	19	21	70			
8	20	21	306			
9	8	11	2			
11,k,2						
1	42	43	238	72	70	239
2	56	51	105	88	91	106
3	55	56	94	96	97	97
4	34	34	286	60	59	285
5	39	39	335	76	74	335
6	-7	4	196			
7	8	7	270			
8	15	16	42			
12,k,2						
0	54	58	107	106	102	103
1	44	43	12	71	73	9
2	27	27	282	44	49	278
3	31	27	357	48	49	358
4	14	12	214			
5	33	32	170	67	66	171
6	18	17	30			
7	12	15	313			
8	-4	4	312			
13,k,2						
1	33	35	130	71	68	133
2	22	21	295			
3	42	45	312	89	88	316
4	-7	8	93			
5	9	9	224			
6	7	9	33			
7	17	21	78			
14,k,2						
0	32	31	9			
1	19	18	313			
2	18	18	199			
3	-7	7	357			
4	-7	4	13			
5	-6	1	336			
6	10	11	104			
15,k,2						
1	22	22	262			
2	32	33	354			
3	30	34	79			
4	10	10	162			
5	-5	8	277			
16,k,2						
0	11	16	100			
1	-6	8	304			
2	19	20	329			
3	-6	7	42			
4	16	18	172			
17,k,2						
1	10	11	23			
2	10	9	33			
3	7	9	189			
18,k,2						
0	6	9	351			
0,k,3						
1	25	29	3	49	47	10
3	13	7	306			
5	27	30	51	37	39	46
7	34	37	245			
9	-6	3	63			
1,k,3						
1	34	40	212	67	60	219
2	58	61	320	101	103	318
3	72	66	30	109	104	33
4	15	11	98			
5	12	12	284			
6	17	11	83			
7	46	46	180			
8	16	18	195			
9	16	16	18			
2,k,3						
0	16	22	53	27	32	49
1	14	13	243			
2	30	29	346	45	44	347
3	71	75	36	113	117	39
4	26	23	208	67	36	208
5	47	46	238	70	70	231
6	30	23	174			
7	-9	9	187			
8	-8	4	23			
9	16	17	101			
3,k,3						
1	68	81	332	119	124	330
2	78	83	32	130	132	33
3	68	69	139	105	105	138
4	90	87	222	140	149	222
5	53	52	186	84	83	177
6	39	41	74			
7	26	23	356			
8	16	13	338			
9	6	8	11			
4,k,3						
0	68	76	28	114	118	23
1	44	46	282	72	69	286
2	18	15	226			
3	40	38	178	58	61	174
4	31	26	236	38	43	230
5	42	37	120	62	58	128
6	-10	11	171			
7	40	41	322			
8	23	22	84			
9	10	18	35			
5,k,3						
1	13	14	111			
2	46	42	144	65	61	134
3	44	44	265	74	67	263
4	35	29	194	57	59	186
5	59	59	67	96	99	67
6	26	23	357			
7	24	27	217			
8	16	15	0			
6,k,3						
0	37	36	267	47	50	271
1	45	40	205	72	64	209
2	35	30	86	45	45	90
3	-10	2	198			
4	27	23	213	30	40	214
5	-10	3	54			
6	36	34	354			
7	12	14	112			
8	9	10	146			
7,k,3						
1	19	15	305			
2	21	19	347			
3	35	35	133	53	57	138
4	44	42	140	72	74	144
5	16	14	263			
6	22	18	297			
7	22	25	353			
8	13	18	290			
8,k,3						
0	35	32	123	50	50	124
1	33	34	247	54	55	251
2	28	28	237	44	43	231
3	12	11	215			
4	37	36	27	60	58	23
5	21	20	96			
6	11	9	187			
7	15	12	353			
9,k,3						
1	32	28	179	48	52	174
2	39	35	83	63	67	74
3	27	22	41	42	40	37
4	35	33	247	66	64	240
5	35	32	316			
6	20	20	14			
7	8	6	132			
10,k,3						
0	36	36	255	66	68	264
1	29	26	332	47	54	326
2	16	15	93			
3	24	23	11			
4	16	14	132			
5	10	10	179			
6	25	27	356			
7	1*	12	212			
11,k,3						
1	27	26	38	55	56	40
2	45	44	10	97	94	13
3	41	42	219	92	92	219
4	19	19	240			
5	16	16	42			
6	12	13	115			
12,k,3						
0	25	25	353	53	52	351
1	19	20	231			
2	-9	7	188			
3	13	16	43			
4	-8	6	151			
5	-6	3	341			
13,k,3						
1	-8	5	33			
2	20	21	228			
3	-7	5	299			
4	12	11	40			
5	-4	4	185			
14,k,3						
0	13	15	303			
1	9	11	58			
2	-7	5	65			
3	-6	2	275			
4	3*	10	145			
15,k,3						
1	9	11	317			
2	8	16	349			

are roughly ten times larger. Vibrational corrections appear to be small, and were neglected.

We find it extremely comforting that the two sets of values agree within their uncertainties. In view of this agreement, we shall discuss the various structural features in terms of the averages of the two sets of values.

These studies have definitely established that, in the crystal state at least, the proton H(13) is attached to N(7) rather than to N(9). In spite of the different numbers of ligands of these two nitrogen atoms, the C(5)–N(7) bond is the same length as the C(4)–N(9) bond and C(8)–N(7) is only slightly longer than C(8)–N(9). Equivalence of the C(4)–N(9) and C(5)–N(7) bonds has also been reported in studies of adenine derivatives (Watson, Sutor & Tollin, 1965; Kraut & Jensen, 1963; Hoogsteen, 1963); in these compounds, however, the C(8)–N(9) bond is considerably longer than in purine. This lengthening is undoubtedly associated with the presence of a substituent group on N(9).

Pullman & Pullman (1958) have carried out a simple Hückel-type molecular orbital calculation for purine; their predicted bond distances are compared with our observed values in Table 6. The maximum difference between the two sets of values, 0·02 Å, is certainly within the range of error to be expected in such a calculation.

Table 6. *Comparison of average observed bond distances with those calculated by the method of molecular orbitals* (*Pullman & Pullman*, 1958)

Bond	*d*(obs.)	*d*(calc.)
N(1)–C(2)	1·349 Å	1·34 Å
C(2)–N(3)	1·332	1·32
N(3)–C(4)	1·337	1·35
C(4)–C(5)	1·403	1·41
C(5)–C(6)	1·389	1·40
C(6)–N(1)	1·330	1·32
C(5)–N(7)	1·374	1·37
N(7)–C(8)	1·330	1·35
C(8)–N(9)	1·312	1·32
N(9)–C(4)	1·374	1·36

Within experimental error, the purine molecule is planar. The least-squares plane, with all heavy atoms weighted equally, was calculated for both sets of parameters; the results are given in Table 7. It is interesting to note that the deviations of the hydrogen atoms from the plane of the heavy atoms are in the same sense for both determinations; however, these deviations are probably not significant.

Packing of the molecules

The structure as viewed down the *c* axis is shown in Fig. 3. Strong N(7)–H(13) · · · N(9) hydrogen bonds, 2·85 Å in length, hold molecules together to form chains along [011], and presumably account for the relatively high melting point of purine (213 °C) com-

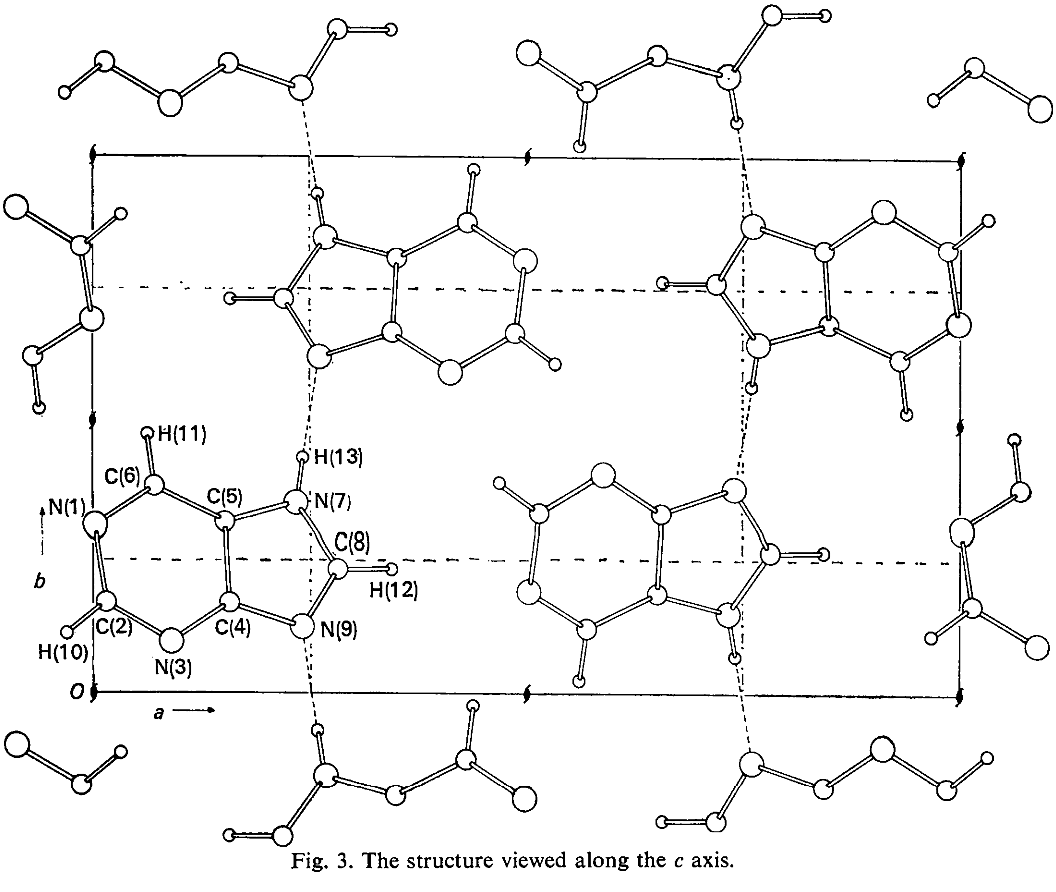


Fig. 3. The structure viewed along the *c* axis.

Table 7. *Deviations of the atoms from the best plane through the ring atoms of purine*

W: $0{\cdot}1852X+0{\cdot}3319Y+0{\cdot}9250Z=1{\cdot}382$ Å
SM: $0{\cdot}1861X+0{\cdot}3390Y+0{\cdot}9221Z=1{\cdot}398$ Å

Atom	W	SM
N(1)	−0·007 Å	−0·001 Å
C(2)	−0·004	0·008
N(3)	0·016	0·004
C(4)	−0·005	−0·008
C(5)	−0·006	−0·009
C(6)	0·006	−0·006
N(7)	0·008	0·015
C(8)	−0·001	0·000
N(9)	−0·007	−0·004
H(10)	−0·17	−0·09
H(11)	0·05	0·11
H(12)	0·10	0·10
H(13)	0·09	0·13

pared with pteridine (140°) and pyrimidine (21°), where there are no opportunities for hydrogen bonds.

As in crystals of other purine and pyrimidine compounds, purine molecules pack on top of one another – in contrast to aromatic hydrocarbons, which tend to form staggered arrays. The interplanar spacing between purine molecules stacked along *c* is 3·39 Å; the shortest interatomic distances between these molecules are N(1) · · · C(6), 3·43 Å, N(3) · · · C(4), 3·46 Å, and C(8) · · · N(9), 3·39 Å. Other short intermolecular contacts are C(2) · · · N(3), 3·48 Å, between molecules related by screw axes and C(6) · · · N(1), 3·47 Å, between molecules related by the *b* glide.

It is pertinent to point out the striking similarity (Fig. 4) between the crystal structures of purine and pyrimidine (Wheatley, 1960). Pyrimidine also crystallizes in space group $Pna2_1$ with *b* and *c* axial lengths approximately the same as in purine; the *a* axis in purine is lengthened to accommodate the five-membered ring. The dimensions of the pyrimidine rings in the two compounds are not significantly different.

Anisotropic thermal vibrations

The magnitudes and directions of the principal axes of thermal vibration have been calculated from the two sets of anisotropic temperature parameters; the results are listed in Table 8. The agreement between the two determinations is not good. In particular, the *B* values of SM are, on the average, about 2 units greater than those of W – an effect which is apparent even at a casual glance at Table 5. We suspect that the disagreement is due in part to the fact that W used a relatively large crystal, for which absorption effects may have been important, but in larger part to the poor quality of crystals obtained by SM, resulting in diffuse high-angle reflections. We take some solace in the observation that the overall patterns of anisotropy are quite similar in the two determinations; and while we have not undertaken a rigid-body treatment of the thermal vibrations, it is apparent that the predominant motions are a lattice vibration parallel to the long axis of the molecule and in-plane libration about the center of mass. This latter motion appears to be too small to affect appreciably the observed bond lengths.

Table 8. *Magnitudes and direction cosines* (*relative to the crystal axes*) *of the principal axes of the thermal vibration ellipsoids*

Atom		Axis i	B_i	C_{ia}	C_{ib}	C_{ic}
N(1)	W	1	3·61	0·895	0·331	0·300
		2	3·15	−0·049	−0·595	0·802
		3	2·49	−0·444	0·733	0·516
	SM	1	5·93	0·978	0·001	−0·210
		2	5·67	0·209	0·070	0·975
		3	4·50	−0·016	0·998	−0·069
C(2)	W	1	4·28	0·884	−0·464	−0·054
		2	2·92	−0·132	−0·359	0·924
		3	2·36	0·448	0·810	0·379
	SM	1	6·35	0·129	0·111	0·985
		2	5·98	0·870	−0·489	−0·059
		3	4·22	0·476	0·865	−0·160
N(3)	W	1	4·17	0·962	−0·269	0·055
		2	2·24	0·047	0·359	0·932
		3	1·42	0·271	0·894	−0·358
	SM	1	6·61	0·966	−0·256	−0·016
		2	4·79	0·119	0·392	0·912
		3	3·13	0·227	0·883	−0·410
C(4)	W	1	2·92	0·882	−0·079	−0·464
		2	2·14	0·401	0·644	0·652
		3	1·54	−0·247	0·761	−0·599
	SM	1	5·89	0·981	−0·043	−0·189
		2	4·52	0·193	0·273	0·942
		3	2·69	−0·011	0·961	−0·277
C(5)	W	1	3·40	0·966	−0·189	−0·177
		2	1·80	0·259	0·707	0·659
		3	1·13	0·001	−0·682	0·732
	SM	1	5·85	0·958	−0·062	−0·281
		2	3·88	0·287	0·295	0·911
		3	2·79	−0·026	0·953	−0·301
C(6)	W	1	3·90	0·947	0·319	−0·033

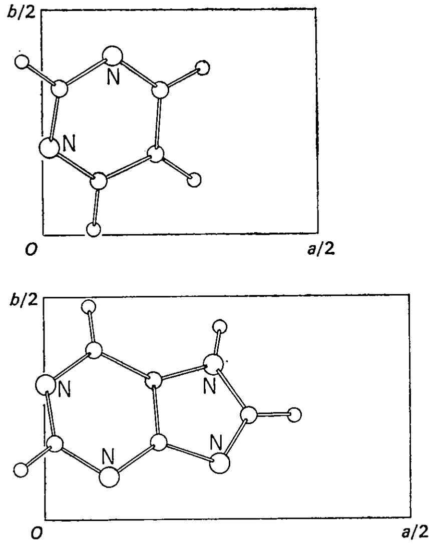


Fig. 4. A comparison of the crystal structures of pyrimidine (top) and purine (bottom). In each case only one asymmetric unit is shown. Nearly exact superposition of the two six-membered rings can be obtained if the origin of either structure is taken at the alternative position $x=\frac{1}{2}$, $y=0$ (see Fig. 3).

Table 8 (*cont.*)

Atom		Axis i	B_i	C_{ia}	C_{ib}	C_{ic}
		2	3·21	−0·076	0·324	0·943
		3	1·65	−0·311	0·891	−0·331
	SM	1	6·86	0·921	0·118	−0·372
		2	5·65	0·332	0·265	0·905
		3	3·20	−0·205	0·957	−0·205
N(7)	W	1	3·65	−0·456	0·301	0·837
		2	2·89	0·769	−0·339	0·541
		3	1·69	0·447	0·891	−0·077
	SM	1	6·17	0·815	−0·361	−0·453
		2	5·20	0·560	0·293	0·775
		3	2·86	0·147	0·885	−0·441
C(8)	W	1	4·40	0·081	0·987	−0·142
		2	3·00	−0·445	0·163	0·880
		3	2·14	0·892	−0·008	0·453
	SM	1	5·26	0·994	−0·112	0·011
		2	4·97	0·056	0·571	0·819
		3	4·47	0·098	0·813	−0·574
N(9)	W	1	3·73	0·878	0·116	−0·464
		2	2·89	0·430	0·235	0·872
		3	1·59	−0·210	0·965	−0·156
	SM	1	5·92	0·949	0·111	−0·294
		2	5·37	0·216	0·447	0·868
		3	3·26	−0·228	0·888	−0·400

One of us (DGW) would like to thank Drs J. Stewart and D. High for the use of their computer programs, the Research Computer Laboratory at the University of Washington for a grant of computer time, and the National Institute of Arthritis and Metabolic Diseases for financial support. He would also like to thank Professor L. H. Jensen for his continued support and encouragement throughout the course of this work.

The work described by SM was carried out as an undergraduate research project (RMS) sponsored by the National Science Foundation.

References

Berghuis, J., Haanappel, IJ. M., Potters, M., Loopstra, B. O., MacGillavry, C. H. & Veenendaal, A. L. (1955). *Acta Cryst.* **8**, 478.

Busing, W. R., Martin, K. O. & Levy, H. A. (1962). U.S. Atomic Energy Commission Report ORNL-TM-305.

Duchamp, D. J. (1964). Program and Abstracts, Amer. Cryst. Assoc. Meeting, Bozeman, Montana; paper B-14.

Hoogsteen, K. (1963). *Acta Cryst.* **16**, 907.

Hughes, E. W. (1941). *J. Amer. Chem. Soc.* **63**, 1737.

International Tables for X-Ray Crystallography (1962). Vol. II, pp. 202–203. Birmingham: Kynoch Press.

Jensen, L. H. (1954). *J. Amer. Chem. Soc.* **76**, 4663.

Kraut, J. & Jensen, L. H. (1963). *Acta Cryst.* **16**, 79.

McWeeny, R. (1951). *Acta Cryst.* **4**, 513.

Pullman, A. & Pullman, B. (1958). *Bull. Soc. Chim. Fr.*, p. 766.

Watson, D. G. (1964). Program and Abstracts, Amer. Cryst. Assoc. Meeting, Bozeman, Montana; paper F-2.

Watson, D. G., Sutor, D. J. & Tollin, P. (1965). *Acta Cryst.* **19**, 111.

Wheatley, P. J. (1960). *Acta Cryst.* **13**, 80.

Acta Cryst. (1965). **19**, 580

Structures Cristallines des Dérivés 2 et 2,3 de la Naphtoquinone-1,4.
II. Chloro-2-hydroxy-3-naphtoquinone-1,4

Par Jacques Gaultier et Christian Hauw

Laboratoire de Minéralogie et Cristallographie, Faculté des Sciences de Bordeaux, France

(*Reçu le 9 février* 1965)

Crystals of $C_{10}O_3H_5Cl$ are monoclinic, space group Pc, two molecules in a unit cell with lattice constants:

$$a=8\cdot25,\ b=3\cdot92,\ c=14\cdot39\ \text{Å};\ \beta=113°\ 20'.$$

Least-squares refinement on visually estimated intensities was used to obtain optimum values for 14 positional and 14 isotropic thermal parameters. The value of R is 0·11.

The molecular packing is discussed in the following article together with that of $C_{10}O_2NH_6Cl$.

Miller (1911) et Fieser (1926) ont montré que les hydroxy-3-naphtoquinone-1,4 sont des mélanges en équilibre de deux formes tautomères: leurs points de fusion varient avec le temps car l'équilibre n'est atteint que lentement à l'état solide et deux éthers peuvent aisément être identifiés. Ils attribuent à ces composés les formules représentées sur la Fig. 1.

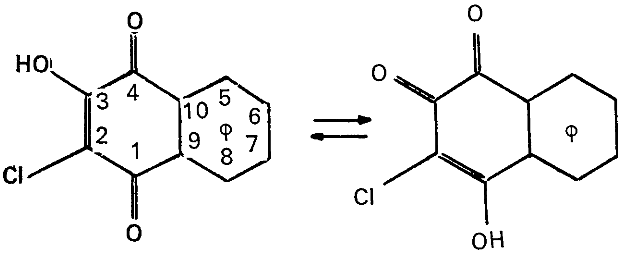


Fig. 1. Formes tautomères de la chloro-2-hydroxy-3-naphtoquinone-1,4.

La chloro-2-hydroxy-3-naphtoquinone que nous étudions ici se comporte comme une antivitamine K et à ce titre peut être comparée à des composés comme la bromo-2-naphtoquinone-1,4 de structure connue.