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The Crystal Structure of 2-(4′-Amino-5′-aminopyrimidyl)-2-pentene-4-one

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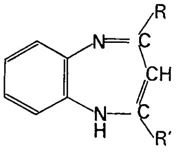
2-(4′-Amino-5′-aminopyrimidyl)-2-pentene-4-one is an aminopyrimidine derivative with a side chain of seven atoms *ortho* to the amino group. The compound crystallizes in the monoclinic space group, $P2_1/c$. The unit-cell dimensions are $a=7{\cdot}024$, $b=12{\cdot}42$, $c=12{\cdot}28$ Å, $\beta=108{\cdot}4°$. Patterson map superpositions and Fourier syntheses led to a trial structure. This structure refined to an R index of 12·8% by Fourier and least-squares techniques. 1005 independent reflections were used.

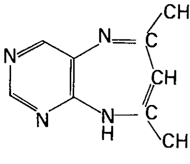
The molecule lies in two planes, one containing the ring and the other containing the side chain. The atoms in the pyrimidine ring have small but significant deviations from the least-squares plane passed through the ring. The packing is characterized by an extensive network of hydrogen bonds. Each molecule participates in four hydrogen bonds between amino nitrogen atoms and neighboring ring nitrogen atoms, and two hydrogen bonds between the side chain nitrogen atom and the oxygen atom. The latter bonds appear to be bifurcated intra- and inter-molecular hydrogen bonds.

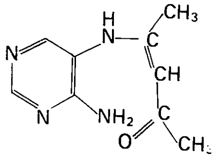
Introduction

The present compound, whose structure has been described briefly elsewhere (Yannoni & Silverman, 1964) was synthesized as part of a program to obtain potential antimetabolites and antitumor agents (Chatterjee, Trites & Modest, 1959, 1964). One hoped to prepare a new aromatic molecule (II) containing a 1,5-pyrimido[4,5-*b*]diazepine ring system in analogy with the 1,5-benzodiazepines (I). The latter are well characterized seven-membered ring structures (Finar, 1958; Barltrop, Richards, Russell & Ryback, 1959; Barltrop, Richards & Russell, 1959).

The present structure analysis establishes that the formation of a seven-membered ring did not occur, and that the reaction product is (III), an aminopyrimidine with a seven atom side chain ortho to the amino group.


I


II


III

Experimental

The crystal used for the determination of unit-cell parameters and for intensity measurements was a thin, yellow platelet. The oval-shaped surface had maximum and minimum dimensions of 0·45 mm and 0·27 mm and the thickness of the sample was 0·05 mm. Unit-cell dimensions were measured on precession photographs (Mo $K\alpha$ radiation).

Crystal data

2-(4′-Amino-5′-aminopyrimidyl)-2-pentene-4-one

$C_9H_{12}N_4O$; $M=192{\cdot}2$, m.p. 180–182 °C.

Monoclinic, $a=7{\cdot}024\pm0{\cdot}009$, $b=12{\cdot}42\pm0{\cdot}04$, $c=12{\cdot}28\pm0{\cdot}02$ Å; $\beta=108{\cdot}4\pm0{\cdot}1°$, $V=1017$ Å^3, $Z=4$.

Absent reflections: $0k0$ when k is odd; $h0l$ when l is odd. Space group is $P2_1/c$ (C^5_{2h}).

Absorption coefficients for X-rays: Cu $K\alpha$, 8·26 cm^{-1}; Mo $K\alpha$, 2·33 cm^{-1}.

Density: $D_{\text{calc.}}(Z=4)=1{\cdot}252$ g.cm^{-3}; $D_{\text{meas.}}$ (flotation) $=1{\cdot}26$ g.cm^{-3}.

Intensity photographs of levels $hk0$ to $hk10$ were taken with Cu $K\alpha$ radiation on Ilford type "G" film using a Weissenberg camera in the equi-inclination geometry. $0kl$ and $1kl$ data were obtained from precession films (Mo $K\alpha$ radiation). All levels were recorded on multiple films and intensities were measured visually by comparison with a calibrated standard. Absorption corrections were not necessary. Lorentz and polarization corrections were applied to all the data. The precession films were used to place all of the Weissenberg levels on a common scale. The scatter in the various film factors and scale factors indicates a precision of about 15% in the final intensities. 1005 independent reflections, 51% of the total number possible, were observed.

Determination of the trial structure

The computation of a Wilson plot (Wilson, 1942) based on the three-dimensional data, determined an overall temperature factor and an absolute scale factor. Smooth curve average intensities as a function of $\sin\theta/\lambda$ computed from the Wilson plot were used to sharpen the coefficients of a three-dimensional Patterson map to atoms at rest.

An extensive combination of Patterson superpositions and Fourier synthesis yielded the trial structure. Separate superpositions were performed on five trial atoms obtained from an analysis of the Harker sections of the Patterson function. Each superposition utilized the three symmetry-related atoms of the trial atom in calculating the minimum function M_4 (Buerger, 1959). Subsequent superpositions based on up to five atoms, *i.e.* up to twenty-fold vector superpositions, suggested by the reasonable looking output of one of the single atom superpositions, failed to resolve the structure. However, a comparison of fifteen distinct superpositions in a search for recurring peaks, the use of stereochemical criteria, and the Harker verifications of the possible atoms, led to a twelve-atom trial fragment. This fragment was subjected to three cycles of least-squares refinement and converged to an R value of 60%. In Table 1, the atoms in this trial structure are compared to their counterparts, if any, in the final refined structure, The Fourier map computed from this twelve-atom fragment did yield enough new information so that in conjunction with stereochemical considerations and one further thirteen-atom Fourier synthesis, all fourteen atoms in the asymmetric unit could be located. This result was obtained despite the fact, as shown by Table 1, that only nine of the fourteen atoms are 'represented' (N(4) and C(4) by two atoms each) and that many coordinates were in error by as much as 0·8 Å.

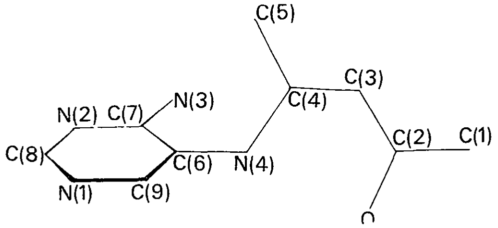


Fig. 1. Conformation and numbering of the atoms in the molecule.

It is significant to compare this with the superposition method. Table 2 lists the input parameters of the best five-atom, *i.e.* twenty-vector superposition computed as part of the search for a trial structure. These are compared with the input parameters of a superposition calculation carried out after refinement was complete. The input parameters here were chosen from atoms in the final structure whose coordinates correspond as closely as possible to the first set of atoms.

In the first superposition, aside from the input atoms, the remaining 16 highest peaks contained only 4 additional correct atoms. In contrast, the output using the 'corrected' coordinates reveals the complete structure. Therefore, in the present analysis, errors in trial atom coordinates proved more damaging in the superposition method than in the Fourier technique. This fact could be attributed to the mathematical stringency of the minimum function conditions, particularly if the Patterson function were over-sharpened. On the other hand, as is well known, the Fourier method requires only that a reasonable number of the strong reflections have correct signs and a very approximate representation of the structure can yield new information. In fact, of the 332 reflections used in the Fourier synthesis computed from the twelve-

Table 1. *Comparison of the twelve-atom fragment (left set of coordinates) with the atoms in the final structure (right set)*

See Fig. 1 for numbering scheme of the final structure.

Input atom	X (30ths)	Y (60ths)	Z (60ths)	Closest final atom	X (30ths)	Y (60ths)	Z (60ths)
1	5	3	16	C(6)	4	5	15
2	27	24	7	N(3)	27	27	7
3	3	0	23	C(7)	3	3	21
4	26	27	14	N(4)	23	31	19
5	3	5	22	N(2)	1	7	25
6	15	27	21	C(4)	18	28	17
7	27	25	2	—	—	—	—
8	17	25	16	C(4)	18	28	17
9	7	4	12	N(4)	6	1	11
10	4	9	14	C(9)	3	12	13
11	19	27	27	C(2)	19	23	28
12	25	2	1	O	25	4	1

Table 2. *Comparison of the input parameters of a five-atom trial superposition (left) with parameters of the five nearest atoms in the final structure*

Input atom	X (30ths)	Y (60ths)	Z (60ths)	Closest atom	X (30ths)	Y (60ths)	Z(60ths)
1	5	3	17	C(6)	4	5	15
2	3	0	23	C(7)	3	3	21
3	27	25	7	N(3)	27	27	7
4	3	5	23	N(2)	1	7	25
5	15	27	21	C(3)	16	25	21

atom fragment, the 207 reflections with correct signs sufficed to produce the full structure in the manner indicated above.

Refinement

The initial stage of the refinement used a single overall temperature factor and 440 strong reflections of low sin θ to which unit weights were assigned. In eight cycles of full-matrix least-squares, the R index decreased from 44% to 18%. The introduction of individual isotropic temperature factors dropped R to 13·4% after four additional cycles. The total shifts in the atomic positions in the course of these twelve cycles constitute the major changes which occurred during refinement, and are listed in the right-hand column of Table 3.

Table 3. *The final positional parameters (P_i), and errors (σ_i), and the total shifts in atomic positions for the first 12 cycles of refinement, all in fractional coordinates*

Atom	Coordinate	P_i	σ_i	Shift
O	x	0·1173	0·0009	−0·004
	y	0·5770	0·0005	0·045
	z	0·4856	0·0005	−0·017
N(1)	x	0·0460	0·0011	−0·054
	y	0·2328	0·0005	0·033
	z	0·7913	0·0007	−0·018
N(2)	x	0·0359	0·0010	−0·063
	y	0·3756	0·0005	0·042
	z	0·9173	0·0006	0·016
N(3)	x	0·1009	0·0010	0·033
	y	0·5524	0·0005	0·044
	z	0·8798	0·0006	0·021
N(4)	x	0·2164	0·0009	0·016
	y	0·4802	0·0005	0·037
	z	0·6859	0·0006	0·016
C(1)	x	0·4391	0·0016	0·058
	y	0·6821	0·0008	0·083
	z	0·4572	0·0010	0·008
C(2)	x	0·3524	0·0013	0·013
	y	0·6117	0·0006	−0·025
	z	0·5308	0·0008	0·007

Table 3 (*cont.*)

Atom	Coordinate	P_i	σ_i	Shift
C(3)	x	0·4672	0·0014	−0·051
	y	0·5879	0·0007	0·029
	z	0·6453	0·0009	−0·008
C(4)	x	0·4046	0·0013	−0·025
	y	0·5244	0·0007	0·032
	z	0·7188	0·0008	−0·023
C(5)	x	0·5427	0·0014	−0·080
	y	0·5006	0·0010	0·035
	z	0·8403	0·0010	−0·069
C(6)	x	0·1486	0·0010	−0·020
	y	0·4098	0·0006	0·041
	z	0·7568	0·0007	−0·006
C(7)	x	0·0949	0·0011	−0·042
	y	0·4455	0·0006	0·056
	z	0·8510	0·0007	0·009
C(8)	x	0·0157	0·0013	−0·047
	y	0·2730	0·0007	0·043
	z	0·8834	0·0008	0·028
C(9)	x	0·1192	0·0013	−0·034
	y	0·3027	0·0006	0·047
	z	0·7290	0·0009	−0.023

At this point, the complete set of 1005 reflections were introduced and assigned unit weights. No unobserved reflections were included in the refinement. The 40 reflections on levels $hk9$ and $hk10$ were rescaled by hand by comparing observed and calculated data. After two cycles, R was 15·1%.

In the final stage, anisotropic temperature factors were introduced. The weighting scheme was determined from the standard deviations: $\sigma = F_o/10$ for $F_o > 10$ and $\sigma = 1$ for $F_o < 10$. Two cycles completed the refinement. The final R index was 12·8% (weighted R was 16·2%). Shifts of the order of 0·01 Å in atomic coordinates occurred during these final two cycles and in the last cycle the changes were 0·5 to 0·1 of the errors in the coordinates. The final positions and the temperature parameters are listed in Tables 3 and 4. The errors calculated from the least-squares equations are also given. Table 5 compares the observed and calculated structure factors.

Table 4. *Final anisotropic thermal parameters based on the expression*

$$T = \exp\{-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl)\}$$

Standard deviations are given in parentheses

Atom	$\beta_{11}10^4$	$\beta_{22}10^4$	$\beta_{33}10^4$	$\beta_{12}10^4$	$\beta_{13}10^4$	$\beta_{23}10^4$
O	274(18)	88(5)	81(6)	−19(8)	52(8)	3(4)
N(1)	331(22)	51(5)	87(8)	−2(8)	80(10)	−4(5)
N(2)	253(18)	45(4)	74(7)	2(7)	63(9)	7(5)
N(3)	271(19)	43(4)	89(8)	0(7)	61(9)	−5(4)
N(4)	182(16)	62(5)	67(7)	−2(7)	55(8)	0(4)
C(1)	386(32)	92(8)	128(12)	−20(13)	116(16)	30(8)
C(2)	228(23)	54(5)	93(10)	−10(9)	74(12)	−4(6)
C(3)	252(23)	75(7)	89(10)	−13(10)	38(13)	−1(7)
C(4)	218(21)	72(6)	101(11)	0(9)	65(12)	10(6)
C(5)	236(23)	152(11)	107(12)	−9(13)	12(14)	34(9)
C(6)	156(18)	55(5)	50(8)	−2(7)	30(9)	−2(5)
C(7)	191(19)	53(5)	59(8)	7(8)	26(10)	0(5)
C(8)	266(24)	56(6)	84(9)	−1(9)	47(12)	−3(6)
C(9)	252(22)	49(5)	107(10)	−1(9)	47(12)	2(6)

Table 5. *Comparison of observed and calculated structure factors*

The three columns of each group contain *h*, $10F_o$, and $8{\cdot}2\,F_c$

h00		
1	465	516
2	593	527
3	241	223-
4	91	84-
5	48	48
h10		
1	24	30-
2	479	470-
3	87	102-
4	172	182-
5	38	44-
6	28	28-
h20		
0	574	522
1	337	317-
2	247	242-
3	368	334-
4	91	91-
6	34	41-
h30		
1	230	241
3	142	141
7	33	22
h40		
0	240	176
1	78	74
2	69	81
4	67	69
6	56	74-
h50		
3	38	26
4	57	48-
h60		
0	319	258-
1	327	294-
2	67	60-
4	33	40
6	60	64-
h70		
1	28	32-
2	20	30
3	113	121
5	37	49
h80		
1	33	29-
2	48	50
3	152	170
4	101	110
5	73	84
6	42	30
h90		
1	41	32-
3	28	36
5	65	74-
6	41	44-
7	40	39-
h 10 0		
0	45	53
1	98	100-
2	37	31-
3	42	47-
h 11 0		
1	37	36-
2	101	107-
3	28	30
h 12 0		
1	66	67-
2	24	26-
3	65	62-
h 13 0		
2	33	41-
3	45	47
h 14 0		
1	20	27
h 15 0		
1	22	21-
h 1 1		
0	117	147
1	937	884-
-1	209	189
2	649	542-
3	294	261-
-3	46	62
4	24	10
-4	43	24-
5	110	103
-5	122	90
6	38	37
-6	74	76
7	31	23
-7	50	57-
h 2 1		
0	221	242-
1	34	44-
-1	792	733-
-2	144	127
3	167	176
-3	58	78-
-6	120	53-
-7	74	77-
h 3 1		
0	195	159-
1	116	91
-1	453	409
2	90	62-
-2	129	104-
3	80	92
-3	47	44
4	117	107
-4	67	64
5	42	50
-5	112	103
6	34	34-
-6	89	82
7	30	32
-7	38	39-
h 4 1		
0	134	111
1	36	39-
-1	256	266-
2	222	214
-2	87	82
3	24	12-
-3	60	44
4	55	51-
-4	10	7
5	57	58-
-5	26	27
6	10	4-
7	22	25
h 5 1		
0	43	83-
1	78	55
-1	162	135
2	50	32
-2	84	69
3	119	119
4	31	26
6	95	86-
7	66	48
-7	46	47-
h 6 1		
1	92	83-
-1	80	78
2	57	59
-2	152	131
3	26	25
-3	104	109
4	66	67-
-4	64	66
5	34	24
-5	10	11
h 7 1		
0	71	65-
1	78	74
2	86	72
-2	93	99-
3	171	147
-3	31	31-
4	34	32-
5	37	51-
6	111	95-
-6	50	57
h 8 1		
0	17	18
1	61	50-
-1	124	128
4	53	60-
-4	93	107-
7	30	26
-7	58	61
h 9 1		
0	40	24
-2	119	104-
3	37	52
-3	61	62-
4	31	31-
-4	123	135-
-5	60	65-
h 10 1		
0	30	14
1	42	39-
-1	26	14
2	26	16-
-2	41	40
3	31	22
-4	135	141-
5	31	11-
-6	33	30-
h 11 1		
0	160	134
1	34	32
-1	74	68
2	41	39
-2	70	69
h 12 1		
0	34	44-
1	43	46-
-1	66	66-
2	30	12-
-2	60	63
3	67	64
h 13 1		
1	69	67
-3	75	66-
-4	24	16-
4	30	27
h 14 1		
2	60	49
-2	44	41
h 15 1		
2	36	39-
-2	22	18
h 0 2		
0	218	302-
1	144	137-
-1	317	254-
2	344	328
-2	613	611-
3	287	296
-3	140	131-
4	235	249
-4	247	247-
5	26	37
-5	30	21
6	84	73
-6	34	43
7	31	39-
-7	26	11-
-8	50	53-
h 1 2		
0	237	353
1	578	601
-1	204	144-
2	447	405
-2	115	103
3	273	270
-3	34	35
4	60	60
-4	162	144
-5	90	91
-6	45	54
-7	20	8-
h 2 2		
0	108	108-
1	325	299
-1	749	493
2	215	220
-2	414	280-
3	62	74
-3	24	36
4	78	84
-4	189	162-
5	114	127-
-5	55	56
6	30	4-
-6	82	95
7	47	51-
-7	50	49
h 3 2		
0	20	30
1	43	10-
-1	738	551-
2	151	168
-2	64	55-
3	140	137-
-3	97	104
4	112	111-
-4	83	91
5	136	152-
-5	106	110
-7	24	24-
h 4 2		
0	492	487-
1	102	94-
-1	66	37
2	53	51-
-2	60	84-
3	38	38-
-3	123	138-
4	42	57
-4	91	94-
5	66	79-
-5	28	28-
-6	40	37
-7	40	46
h 5 2		
1	57	62
-1	219	180-
2	314	327
-2	135	139-
-3	58	65
4	24	24
-4	22	2-
5	22	4
6	24	18
-6	43	34-
7	24	25
h 6 2		
0	76	70-
1	67	68-
-1	206	166
2	24	11-
-2	335	287
-3	76	73
-4	42	44
5	47	57-
-5	26	36-
-7	26	16
h 7 2		
0	260	259-
1	114	109-
-1	31	46-
-2	158	153-
3	37	39-
4	57	48-
-4	43	36-
-5	78	85-
6	28	25-
h 8 2		
0	26	24-
1	33	38-
-1	156	143
-2	30	31
-3	95	99
-4	77	88-
-5	66	72-
6	33	31
-6	31	18-
-7	31	33-
h 9 2		
-1	173	159
-2	97	98
-3	155	151
-4	69	72-
5	50	52
6	17	21
h 10 2		
0	30	19-
1	91	103-
-1	60	47
2	34	37-
-2	86	84
-3	154	160
-4	33	35
h 11 2		
1	30	17
2	26	17
-2	37	35
-3	61	56
-5	28	32
h 12 2		
1	26	25-
2	38	45-
3	58	59-
4	22	22-
5	24	24-
-5	20	24
h 13 2		
1	28	8-
-1	44	48-
2	26	18
4	20	26-
h 14 2		
-1	22	8
2	69	10-
h 1 3		
0	523	310
1	298	253
-1	33	51
-2	170	150
3	129	98-
-3	41	30
4	264	238-
-4	60	67
5	103	100-
-5	34	26-
6	47	0
-6	38	43
-7	31	20
-8	47	39-
h 2 3		
1	241	154
-1	263	321-
2	100	95-
-2	272	264-
3	138	145-
-3	162	154-
4	124	118-
-4	109	120-
5	100	102-
6	54	48
h 3 3		
1	123	119
-1	96	116
-2	278	283
3	78	73-
-4	70	61-
5	38	42-
-5	180	175-
6	57	47
-6	100	107-
-8	20	21-
h 4 3		
0	246	185
1	122	109
-1	69	69-
2	145	150
-2	24	8-
-3	155	170
3	132	125-
-4	90	78
5	47	35-
-5	70	67
h 5 3		
0	161	154-
1	131	106-
-1	301	297-
2	112	103
-2	367	358
3	72	69
-3	84	110-
4	79	79
-4	107	103
-5	98	104-
-7	41	56
h 6 3		
0	30	17
1	192	182
-1	78	96
2	96	85
-2	90	114-
3	66	64-
4	36	39-
-4	72	66
-5	87	99-
h 7 3		
0	120	114-
1	142	145-
-1	96	119-
2	40	41
-2	122	149
3	41	43
4	40	42
-5	93	104-
h 8 3		
0	28	25-
1	57	75
-1	117	129
-2	24	30
3	28	13
-3	100	115
4	38	38
-4	105	123
5	36	40
-5	28	32-
h 9 3		
0	80	89-
1	58	76-
-1	83	102-
2	38	41
-2	55	67-
3	45	41
-3	61	78
4	34	3-
-4	45	47
-5	53	65
-6	84	91
-7	43	48
h 10 3		
0	89	101-
1	70	78-
-1	114	120-
2	73	83-
-2	89	99-
3	46	46-
-3	45	40-
-4	44	46-
-5	33	35-
h 11 3		
0	28	27-
1	36	38
-1	95	102-
2	61	68
-2	115	116-
3	46	61
-3	67	71-
-4	10	23-
5	22	20
-5	22	20
h 12 3		
0	46	59
1	76	77
3	26	3-
h 13 3		
-5	34	30
h 14 3		
-2	41	38-
3	24	26-
h 0 4		
0	20	62
1	145	130
-1	386	353-
2	261	285-
-2	267	354-
3	58	55-
-3	158	176-
4	273	256-
-4	60	50
5	149	130
6	26	39
-6	60	60
7	20	37
-7	28	9
-9	24	26-
h 1 4		
0	63	79-
1	95	66
-1	108	78
2	143	153-
-2	42	60
3	22	20
-3	144	129
6	40	52
-6	31	38-
7	30	7
-7	36	37-
h 2 4		
0	144	140-
1	137	121
-1	160	206-
2	137	118-
-2	153	164-
3	55	47
-3	131	118
4	50	37-
-4	124	125
5	160	150
-5	87	85
6	67	70
7	38	35
h 3 4		
1	158	157
-1	30	31-
2	20	35
3	116	105
-3	202	202
4	81	66
-4	28	42
-5	65	73
6	48	43
-6	73	71-
7	28	23-
h 4 4		
0	105	103-
1	70	65
-1	220	174-
2	47	40-
-2	220	226
-3	114	136
4	47	47-
-4	191	185
-5	66	65
6	31	32-
-6	56	60-
h 5 4		
0	174	176-
1	101	101-
-1	182	149-
2	106	110-
-2	106	110-
3	58	65-
-4	92	115
5	38	13
-5	31	33
h 6 4		
0	24	21-
1	47	58
-1	172	169-
2	97	92
-2	136	152
3	97	95
-4	46	52
-5	79	87-
-6	74	81-
h 7 4		
0	53	46-
1	40	41
-1	72	78
2	87	89-
-2	42	38-
3	36	42-
-3	78	93-
-4	123	126
-5	43	40-
-6	31	28
h 8 4		
2	42	27
-3	57	57
-4	50	56-
-5	94	97-
-6	46	55-
-7	33	32-
h 9 4		
0	48	52
-1	31	28-
2	28	8-
-2	31	30-
-3	86	89-
4	40	29
-4	51	60
-6	43	42
-7	22	6-
h 10 4		
0	122	118
1	114	112
-1	72	69
-2	42	45-
-3	68	68-
4	80	71-
-4	81	88-
-5	77	73-
-6	20	2
h 11 4		
0	115	95
1	60	52
-1	63	53
2	54	49-
-2	57	51
-3	10	26-
h 12 4		
0	54	44
1	82	77
-1	82	79
-2	31	30
h 13 4		
2	62	47-
-2	31	26-
h 14 4		
0	24	19-
h 1 5		
0	427	477
1	145	181
-1	151	160
2	74	68
h 1 5		
-2	300	235-
3	31	33-
-4	40	39-
5	67	73
-5	34	30
7	24	30-
-8	45	46
h 2 5		
0	185	226-
1	43	47
-1	149	162-
2	60	68-
-2	129	91-
-3	288	225
3	105	112
4	46	46-
-4	90	73
5	42	44-
-5	123	122
7	24	30-
-7	44	44-
h 3 5		
-1	233	195-
2	34	36
-2	533	422-
3	68	76-
-3	109	81-
4	42	47
-4	159	147-
-5	110	115
-6	80	80-
h 4 5		
1	82	85
-1	288	215-
2	106	109
-2	183	158-
3	106	114
-3	103	73-
4	28	24-
-4	83	76-
5	31	36-
-5	45	40
6	43	42-
-6	88	76-
h 5 5		
0	69	75
1	52	54
-1	24	23-
-2	31	30
2	24	24
3	30	38-
-3	17	12
4	40	36
-4	24	19-
-5	58	58
-6	106	103-
h 6 5		
0	42	37
1	61	45
-1	117	102
2	52	38
-2	74	58
3	59	50
-3	45	41-
-4	76	66
-8	28	28-
h 7 5		
0	88	86-
1	93	106-
-1	70	60-
-2	66	55-
3	36	44-
-3	118	122
-4	34	45
-5	82	85
h 8 5		
0	67	81
1	22	27-
-1	36	33
-2	36	26-
3	28	17-
-3	212	204-
-4	101	101-
-5	44	38-
6	17	1-
-7	33	30
h 9 5		
0	67	74
1	31	29-
-1	130	124
-2	83	88
-3	176	182
-4	42	67
5	30	33
-5	34	32
h 10 5		
0	97	105
1	76	69-
-1	31	23
2	64	70-
-2	97	100
-3	31	33-
-5	69	68
-6	60	53
h 11 5		
0	72	71-
1	103	96-
-1	36	38-
2	130	117-
3	52	57-
-3	31	17-
4	30	29-
-5	28	31-
h 12 5		
0	33	26-
1	50	46-
-1	37	20-
2	63	60-
3	34	32
-4	26	27-
h 13 5		
0	22	8-
1	28	33
-1	34	36
-2	26	19
-3	30	20
h 0 6		
0	90	85
1	281	273-
-1	83	69-
2	84	95-
-2	120	86-
3	113	121-
-3	143	128-
-4	160	158
-5	81	74-
-6	30	28
-7	168	175-
-8	70	67-
h 1 6		
0	45	59-
1	101	112
-1	55	81-
2	36	38
-2	169	145-
3	89	81
-3	42	34
-4	43	37-
-7	74	79-
-8	20	26-
h 2 6		
0	177	229
1	64	70-
-1	183	169
3	101	110-
-3	52	25
-4	84	83
-5	73	78
-6	38	45
-7	71	74-
h 3 6		
0	17	28
1	54	61
-1	141	117-
2	36	38
-2	60	32-
3	40	48
-3	81	82
4	75	83-
-5	50	43
-7	44	45-
h 4 6		
0	90	108
-1	157	144
-2	83	83
3	30	27-
-3	26	33-
4	80	67
-4	42	47-
-5	50	43
h 5 6		
0	31	31
1	31	27-
2	31	30
-1	45	30
-2	129	116
-3	72	65
4	62	62-
-4	26	26
h 6 6		
1	40	32-
-1	89	73
-2	50	44
4	44	40
-5	30	26
-7	26	25
h 7 6		
0	59	56-
1	103	106-
-1	88	84
-2	76	77
3	34	39-
-3	42	37
-7	42	43
h 8 6		
0	10	34-
1	64	69-
-1	58	62-
2	45	45
-2	166	171-
-3	92	91-
4	30	24
-4	105	115-
-5	38	24-
-7	37	27
h 9 6		
0	82	82
1	97	101-
-1	74	64
-2	122	120
4	31	27
-4	110	112-
-5	46	45-
-6	41	40-
h 10 6		
1	51	50-
-1	67	66-
2	33	35
-2	30	19-
3	33	37
-4	44	46
-6	37	33
h 11 6		
1	51	47-
-1	53	44-
3	44	44
-3	33	26-
4	17	17
-4	63	66-
-6	28	23
h 12 6		
0	31	29
1	46	44
-1	36	30-
2	47	43
-2	31	2
3	31	33
-3	42	39-
h 13 6		
2	24	21
h 1 7		
0	50	50-
1	50	44
-1	31	21-
2	51	49
-2	151	166-
3	77	67
-3	230	168-
-4	91	110
-5	46	44
-6	209	188
-8	58	61-
h 2 7		
0	43	38
1	95	83
-1	24	24-
2	45	40
-2	20	17-
3	52	40
-3	126	115
4	37	37-
-4	20	22
-5	26	27
-6	109	96
-8	67	62
h 3 7		
0	103	109-
-1	92	84
2	69	79-
-2	34	23
-3	50	30-
-4	24	36-
-5	31	35
-6	70	57
h 4 7		
0	85	100-
1	78	80-
-1	202	170-
-3	74	62
-4	70	61
-5	28	9-
-6	34	29
-8	28	26
h 5 7		
0	242	249-
1	54	52-
-1	22	8
2	128	143-
-2	31	47
3	85	80
-3	74	56-
4	33	20
-4	55	55-
-5	60	64-
-8	30	21
h 6 7		
0	114	122-
1	42	48
-1	31	30-
2	104	104
-2	104	96-
3	42	41
4	44	44
-5	53	53-
h 7 7		
1	46	43
-1	263	239
2	30	20-
-2	183	149
3	55	50
-3	112	102
-4	47	43-
-5	72	76-
h 8 7		
0	135	134-
1	72	67-
-1	22	10-
-2	37	25-
3	28	22-
-3	78	79
-4	24	0
h 9 7		
0	24	28
1	30	9-
-1	56	55
-4	53	48-
-5	67	61-
-6	28	13-
h 10 7		
0	34	32
-1	42	33
2	37	38
-2	59	55
-3	83	73
-5	20	3
-6	26	20
h 11 7		
0	61	53
1	37	35
-1	36	23
-2	36	22
-4	26	32
-6	36	29
h 12 7		
-1	20	11
-4	45	43-
-5	31	20-
h 13 7		
-1	24	31-
-4	43	32-
h 14 7		
-1	31	19
-2	17	11
h 0 8		
0	105	111
1	125	97
-1	73	82
2	68	61
-2	33	21-
3	54	57-
h 0 8		
3	54	57-
-3	97	84-
4	92	65-
-4	34	23-
5	67	50-
-6	94	105
-7	135	138
h 1 8		
0	73	65-
1	67	58-
-1	77	94-
2	58	39-
-2	83	106-
-3	30	34-
-4	107	109-
-5	106	108-
-6	44	41-
h 2 8		
1	53	31
2	62	47
-3	75	69-
-4	148	154-
-5	81	83-
-6	75	79-
h 3 8		
0	58	51
-1	87	83-
2	76	67
-2	60	57
-3	54	67
-4	33	30
-5	90	90-
-7	67	49-
h 4 8		
0	46	46-
1	70	53
2	48	32
-2	159	151
3	80	76
-3	63	56
-5	43	17
-6	38	21-
-7	41	33
h 5 8		
1	62	62
-1	50	43-
2	38	42
-4	55	42
5	34	24-
-5	79	76-
h 6 8		
0	128	140-
-2	66	61
3	77	73
-5	59	50-
h 7 8		
1	156	152
-1	120	129
2	59	43
-2	37	11-
3	36	23-
-3	48	38
-5	31	4-
h 8 8		
0	91	96-
1	97	108-
2	10	31-
-2	50	42
-3	137	115
-4	54	50
-5	43	34
-7	44	40
h 9 8		
0	63	45-
-1	44	53-
-2	108	96-
-3	31	39-
h 10 8		
-2	43	23-
h 11 8		
-5	37	28-
h 13 8		
-3	51	45
h 1 9		
-3	76	92
-5	61	43-
h 2 9		
-2	58	59
h 2 9		
-3	173	179
-4	99	108
h 3 9		
-1	101	132-
-2	78	79
-3	84	74
-4	57	54
-5	73	65
h 4 9		
-1	96	104-
-2	57	65
-3	44	42
-4	112	138
h 5 9		
-1	85	88-
-2	91	89
2	81	91-
h 0 10		
1	91	101
-1	32	38
-3	111	117
-4	138	136
-5	68	67
h 1 10		
-1	26	24-
-2	37	36-
-3	98	96
-4	62	49
-5	103	102
-6	65	54
h 2 10		
-1	85	100-
-2	173	182-
-5	84	76
h 3 10		
-1	141	163-
-2	146	167-
-3	64	78-
-4	44	62-
h 4 10		
0	59	58
-4	46	50-
h 5 10		
-4	56	60
-5	70	68
-6	48	25

A difference Fourier synthesis was computed from the F values in Table 5 in an attempt to locate the 12 hydrogen atoms. 13 peaks, all rather diffuse, had the requisite height for hydrogen atoms but only six were reasonable stereochemically. Most of the spurious peaks were grouped about the methyl carbon atoms suggesting free rotation of the methyl groups which are in open parts of the structure. No further attempts were made to determine the positions of the hydrogen atoms.

Discussion

Conformation of the molecule

The bond lengths and bond angles of the molecule are shown in Fig. 2. The standard deviations in these dimensions, calculated from the variance–covariance matrix computed from the least-squares equations and from the errors in the unit-cell dimensions, are included in parentheses. Typical values of the standard deviations are 0·01 Å for the bond lengths and 0·8° for the bond angles*.

The molecule lies approximately in two planes: the pyrimidine ring plane which includes the amino nitrogen atom (N(3)) and the side chain nitrogen atom (N(4)); and the plane of the side chain atoms including the ring carbon (C(6)). The extent of planarity was analyzed by the method of Schomaker, Waser, Marsh & Bergman (1959). The equation of the least-squares plane through the six ring atoms is $5{\cdot}661\ x-2{\cdot}294\ y+3{\cdot}431\ z-2{\cdot}473=0$ where x, y, and z are fractional coordinates of the cell edges. Deviations ($\Delta_\perp$) from this plane in Å, and in number of standard deviations are listed in Table 6. In the present results $\sigma_\perp \doteq \sigma x \doteq \sigma y \doteq \sigma z$. Also given are the results of the analysis of side chain planarity. The equation for the least-squares plane through all seven side chain atoms is $-3{\cdot}392\ x+10{\cdot}009\ y+5{\cdot}661\ z-7{\cdot}998=0$.

Table 6. *Analysis of the planarity of the pyrimidine ring and of the side chain*

Atoms in parentheses determined the least-squares planes. (See text for explanation).

Pyrimidine ring			Side chain plane		
Atom	$\Delta_\perp$ (Å)	$\lvert\Delta_\perp/\sigma_\perp\rvert$	Atom	$\Delta_\perp$ (Å)	$\lvert\Delta_\perp/\sigma_\perp\rvert$
(C(6))	0·025	3·1	(N(4))	0·010	1·5
(C(9))	0·009	1·1	(C(4))	0·004	0·5
(N(1))	−0·032	4·0	(C(5))	−0·017	1·5
(C(8))	0·021	2·6	(C(3))	0·017	1·9
(N(2))	0·016	2·0	(C(2))	−0·001	0·2
(C(7))	−0·038	4·8	(C(1))	−0·001	0·1
N(3)	−0·151	18·9	(O)	−0·014	2·2
N(4)	0·004	0·5	C(6)	−0·079	11·3

The pyrimidine ring has significant deviations from planarity; the side chain has deviations from planarity of doubtful significance. The amino nitrogen atom is 0·15 Å from the plane of the ring, slightly more than the deviation occurring in the structure of 4-amino-2,6-dichloropyrimidine (Clews & Cochran, 1949) in which the amino nitrogen atom is 0·10 Å from the pyrimidine ring. Space-filling molecular models indicate that the deviations of the amino nitrogen atom (N(3)), the adjacent ring carbon atom (C(7)), and the methyl carbon atom (C(5)) from their respective planes, are in the sense which relieves steric strain arising from the methyl hydrogen atoms.

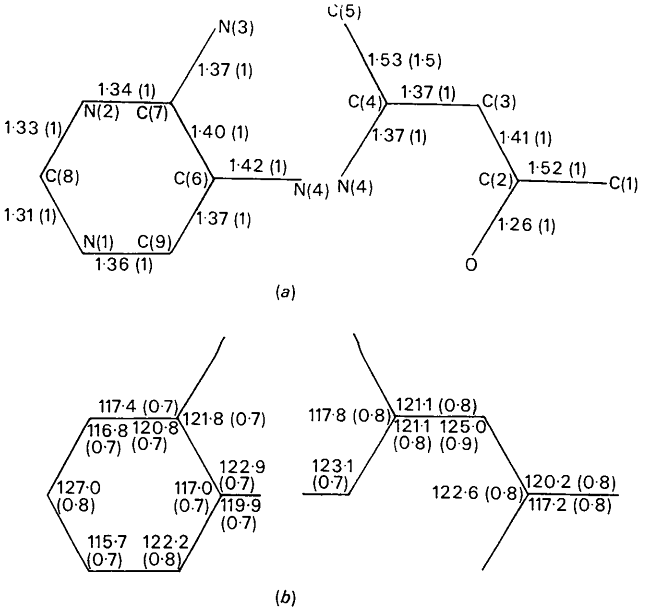


Fig. 2. Dimensions of the molecule: (*a*) Bond lengths in Å; standard deviations in units of 0·01 Å in parentheses; (*b*) Bond angles in degrees; standard deviations in degrees in parentheses.

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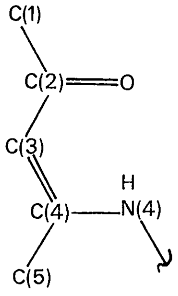
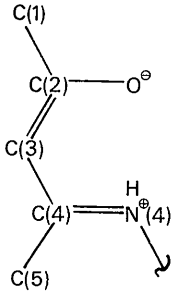
* The standard deviations cited in the earlier communication (Yannoni & Silverman, 1964), are incorrect.

There are few data of high accuracy available on the dimensions of the pyrimidine ring as it is found in pure pyrimidine (Wheatley, 1960), or in the aminopyrimidines (Clews & Cochran, 1948, 1949). Several accurate determinations have been carried out on compounds in which the pyrimidine ring is fused to a five-membered ring or in which there is substitution on the carbon atom bonded to the ring nitrogen atoms (Hoogsteen, 1963). However, these are cases in which the ring dimensions are quite different. In Fig. 3, the ring as found in the present compound is compared with the structure of pure pyrimidine determined at −20 °C (Wheatley, 1960). Wheatley estimates errors of ±0·007 Å and ±0·5° in the bond lengths and bond angles respectively, as well as an additional uncertainty of ±0·015 Å in the bond distances as a result of thermal motion. Also included for comparison are the bond-lengths for 4-aminopyrimidine calculated by simple valence bond theory (Pauling, 1948) as computed by Clews & Cochran, who employed charged resonance forms involving double bonds between the ring-carbon and its adjacent amino nitrogen atom. Despite the presence of the bulky side chain and the *ortho* amino group, the ring dimensions of the present compound do not differ significantly from those found in pure pyrimidine.

Several of the side chain atoms participate in bonds having mixed character. A valence-bond calculation based on Pauling's equation (1948, p. 195) was performed with the use of the standard values: C——C 1·54 Å, C══C 1·33 Å, C——N^+ 1·45 Å, C══N^+ 1·24 Å, C——O^- 1·45 Å, C══O 1·22 Å. A 'mixture' of two-thirds of the ketonic form of the molecule (IV) and one-third of the charged resonance form (V) gives the reasonable correlation shown in Table 7. Assuming the predominance of the enolic form, one obtains a similar fit, but only by assuming a two-thirds contribution of the charged resonance form. This calculation, the N · · · O hydrogen bond distance (see below), and a peak in the questionable final difference Fourier map, all indicate that the molecule is largely in the keto form. On the other hand, spectral results taken in a potassium bromide pellet and in solution (Chatterjee, Trites & Modest, 1964) point to the predominance of the enolic form.



IV



V

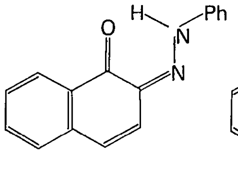
Table 7. *Results of simple valence-bond calculation on bond distances in the side chain*

Bond	$D_{\text{calc.}}$	$D_{\text{obs.}}$
C(4)–C(5)	1·54	1·530
C(2)–C(1)	1·54	1·517
N(4)–Ring	1·46	1·418
N(4)–C(4)	1·33	1·369
C(3)–C(4)	1·36	1·371
C(3)–C(2)	1·42	1·414
C(2)–O	1·24	1·255

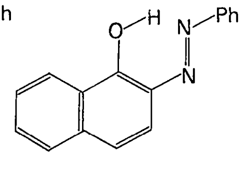
Another possibility is that both tautomeric forms are present, either in dynamic equilibrium across the N(4) · · · H · · · O hydrogen bond, *i.e.* 'mesohydric tautomerism' (Hunter, 1945), or in a static equilibrium throughout the crystal, an order-disorder condition. The results on 1:4-naphthaquinone phenylhydrazone (Hadži, 1956) are pertinent to the present compound. For that compound, spectral evidence in the solid established the presence of the tautomeric forms (VI) and (VII). Hadži asserts that crystallographic information might not yield an unambiguous result in this case since (VI) and (VII) would be expected to have similar bond lengths as a result of contributions from charged resonance forms analogous to (V). He adds that the proton would be expected to change back and forth from oxygen to nitrogen with time, and consequently both molecules would have the same dimensions.

Molecular packing

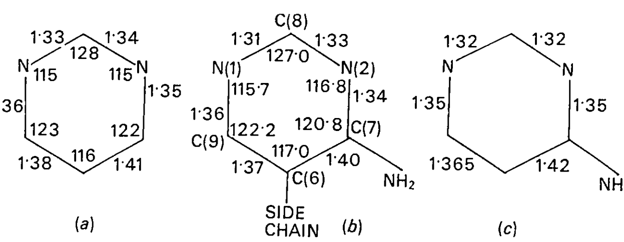
There is an extensive network of hydrogen bonding linking the molecules. Each molecule participates in



VI



VII



(*a*) (*b*) (*c*)

Fig. 3. Comparison of the dimensions of the pyrimidine ring in (*a*) pure pyrymidine, (*b*) present compound, and (*c*) as calculated for 4-aminopyrimidine.

six hydrogen bonds. The amino nitrogen atom takes part in two bonds, and the other three nitrogen atoms and the oxygen atom take part in one bond each.

Fig. 4 depicts the hydrogen bonding between the nitrogen and oxygen atoms of two molecules related by a center of symmetry. There are intramolecular and intermolecular N · · · O distances of 2·673 and 2·984 Å respectively. The molecular geometry satisfies the conditions (Pauling, 1948) for an intramolecular hydrogen bond; namely that the hydrogen atom is part of a six-membered ring. The intermolecular distance agrees closely with other N–H · · · O bonds (Wallwork, 1962) but is somewhat long for a N · · · H–O bond. The small square in Fig. 4 indicates the position of the nearest peak of requisite height for a hydrogen atom in the final difference Fourier synthesis. This peak, about 1·05 Å from the nitrogen atom, indicates the predominance of the keto form of the molecule and also suggests a bifurcated hydrogen bond (Nakamoto, Margoshes & Rundle, 1955) involving inter- and intra-molecular bonding. However, one cannot place great confidence in the difference Fourier synthesis because of several significant peaks which occur in impossible positions.

The intermolecular carbon–oxygen distance of 3·17 Å between O and C(9) is comparable to similar distances some of which are hydrogen bonds (Sutor, 1963). Recently, a 3·11 Å contact was observed in 1-methylthymine (Hoogsteen, 1963); there is also one of 3·19 Å in uracil (Parry, 1954). The identical carbon atom of the pyrimidine ring is involved in all three cases. However, if the hydrogen atom in question were in the plane of the pyrimidine ring, the C——H · · · O bond angle would be about 90° and the H · · · O distance would be well over the sum of the van der Waals radii, eliminating the possibility of a hydrogen bond.

In addition to the side-chain hydrogen bonding, hydrogen bonds join the pyrimidine rings. Each of the two amino hydrogen atoms is bonded to ring nitrogen atoms of other molecules, a common arrangement in aminopyrimidines (Clews & Cochran, 1948, 1949; White & Clews, 1956). The distances and angles are shown in Fig. 5. The N–H · · · N distances of 3·021 and 3·073 Å are in the range of other hydrogen bonds of this type (Wallwork, 1962). Molecules II and III are related to molecule I by a center and a twofold screw axis, respectively. All three rings are almost coplanar and make an angle of about 50° with the *a* axis. The final difference Fourier synthesis has two peaks of reasonable height for hydrogen atoms which lie along the lines joining the nitrogen atoms and at the expected distance from the amino nitrogen atoms.

The overall molecular packing is illustrated in Fig. 6. The structure consists of infinite, approximately parallel, two-dimensional networks of pyrimidine rings in the plane at $x=0$. Each molecule is joined to three neighboring molecules in the same network by N——H · · · N bonds of the type depicted in Fig. 5. Also, each molecule is connected to a fourth molecule in this network by the side chain hydrogen bonding illustrated in Fig. 4. The space between the pyrimidine ring networks is filled by the side chain atoms, the planes of which assume orientations of approximately 45° and 135° with the *b* axis.

There are no other intermolecular contacts of particular interest.

Anisotropic thermal motion

In Table 8 are listed the r.m.s. components of thermal displacement for each atom along the three principal axes of the ellipsoid which characterizes its anisotropic thermal motion (Busing & Levy, 1958). The directions of the principal axes, defined by angles made with the axes x', y', and z', are also given. The orthogonal set x', y', z', is defined by the orientation of the pyrimidine ring whose coordinates are given in Table 3. The vector from N(1) to C(8) defines the x' axis; the vector perpendicular to the ring (defined by the cross product of x' and the vector from C(6)

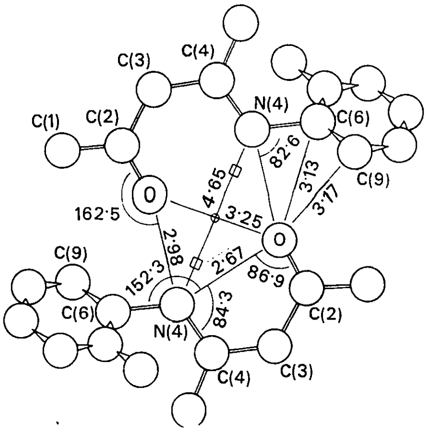


Fig. 4. Hydrogen bonding in the side chain, and other intermolecular contacts between two molecules related by a center of symmetry.

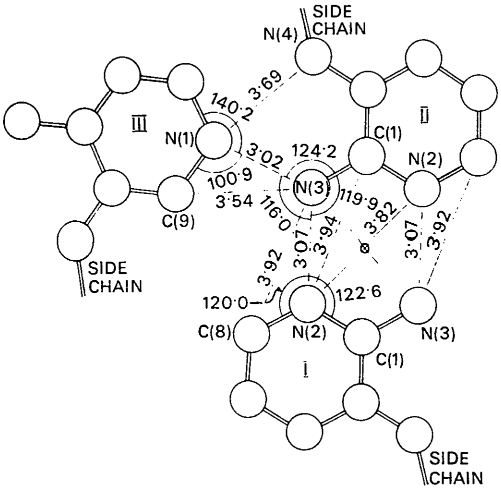


Fig. 5. Hydrogen bonding (dotted lines) and other intermolecular contacts between pyrimidine rings.

to C(9) is the y' axis; and the z' axis which completes the orthogonal set lies also in the plane of the ring.

Table 8. *The r.m.s. displacements along, $\mu(R_i)$, and the directions of, $\varphi(R_i, x')$, $\varphi(R_i, y')$, $\varphi(R_i, z')$, the three principal axes of the thermal ellipsoid for each atom*

Atom	R_i	$\mu(R_i)$	$\varphi(R_i, x')$	$\varphi(R_i, y')$	$\varphi(R_i, z')$
O	1	0·226 ± 0·010 Å	130°	96°	41°
	2	0·243 ± 0·009	59°	143°	71°
	3	0·273 ± 0·008	124°	127°	125°
N(1)	1	0·198 ± 0·010	125°	99°	143°
	2	0·224 ± 0·012	36°	87°	126°
	3	0·278 ± 0·010	98°	10°	96°
N(2)	1	0·181 ± 0·011	87°	101°	169°
	2	0·210 ± 0·011	19°	71°	90°
	3	0·246 ± 0·009	109°	22°	101°
N(3)	1	0·182 ± 0·010	122°	100°	146°
	2	0·234 ± 0·011	42°	68°	123°
	3	0·255 ± 0·009	114°	24°	86°
N(4)	1	0·178 ± 0·012	138°	119°	62°
	2	0·220 ± 0·009	58°	91°	32°
	3	0·224 ± 0·010	114°	29°	74°
C(1)	1	0·198 ± 0·017	115°	95°	26°
	2	0·298 ± 0·012	57°	40°	70°
	3	0·325 ± 0·014	136°	51°	106°
C(2)	1	0·196 ± 0·013	71°	64°	148°
	2	0·207 ± 0·012	38°	68°	61°
	3	0·261 ± 0·013	122°	35°	77°
C(3)	1	0·228 ± 0·014	104°	48°	135°
	2	0·247 ± 0·013	106°	49°	45°
	3	0·258 ± 0·015	158°	112°	91°
C(4)	1	0·206 ± 0·013	62°	52°	130°
	2	0·233 ± 0·012	78°	51°	41°
	3	0·270 ± 0·013	149°	61°	100°
C(5)	1	0·219 ± 0·014	101°	11°	91°
	2	0·270 ± 0·016	55°	85°	144°
	3	0·368 ± 0·014	143°	99°	126°
C(6)	1	0·183 ± 0·016	159°	98°	71°
	2	0·188 ± 0·012	77°	159°	74°
	3	0·208 ± 0·010	105°	109°	155°
C(7)	1	0·197 ± 0·012	84°	152°	117°
	2	0·202 ± 0·014	29°	98°	62°
	3	0·218 ± 0·012	118°	117°	41°
C(8)	1	0·208 ± 0·011	121°	97°	148°
	2	0·241 ± 0·014	38°	117°	114°
	3	0·245 ± 0·011	70°	28°	109°
C(9)	1	0·196 ± 0·011	110°	100°	158°
	2	0·238 ± 0·010	101°	162°	75°
	3	0·274 ± 0·013	157°	75°	74°

The methyl carbon atoms, C(5) and C(1), are seen to have the most highly anisotropic thermal motion. A three-dimensional model of the various principal axis directions indicates no obvious rigid body motions with the possible exception of a twist of the side chain about the N(4) — ring bond.

Bond distance corrections necessitated by thermal motion and made on the assumption that one atom 'rides' on another (Busing & Levy, 1959) have magnitudes of about 0·007 Å, while the assumption of complete independence in the motion of the individual atoms leads to increases in the bond distances of about 0·08 Å. Since no clear choice can be made in the range between these extreme assumptions only uncorrected bond distances are reported.

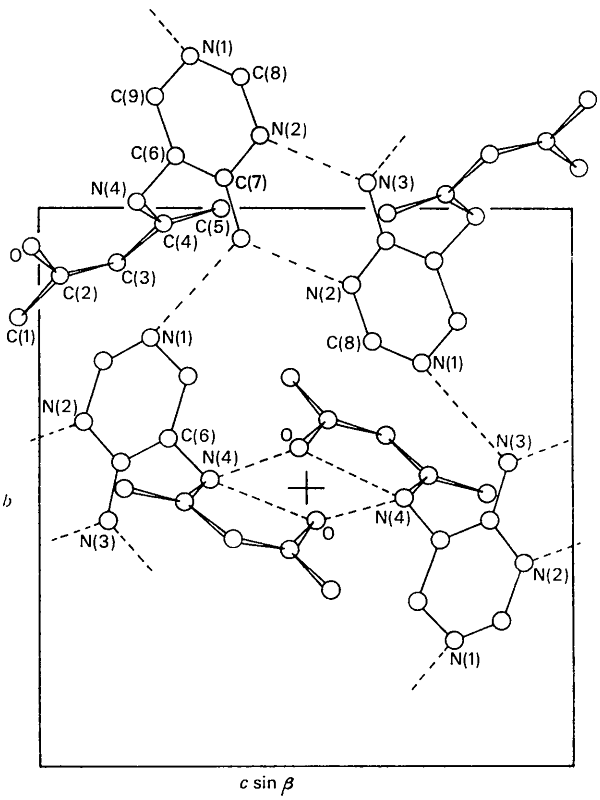


Fig. 6. Projection of the structure down (100). Hydrogen bonds shown as dotted lines.

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Phase Transition and Crystal Structures of Adamantane

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The −65 °C phase transition in adamantane, $C_{10}H_{16}$, involves a change from the face centered cubic room-temperature structure to a tetragonal structure, space group $P\bar{4}2_1c$, with $a=6\cdot60$, $c=8\cdot81$ Å and $Z=2$. The low-temperature cell is related to the cubic cell by $a_{\mathrm{tetr}} \simeq a_{\mathrm{cubic}}/\sqrt{2}$ and $c_{\mathrm{tetr}} \simeq a_{\mathrm{cubic}}$. A single-crystal X-ray study of the low-temperature phase at −110 °C shows the arrangement of the molecules to be unchanged except for a 9° tilt about the *c* axis. A redetermination of the room-temperature structure using single-crystal data supports a disordered structure, space group $Fm3m$, rather than the previously assumed, ordered, $F\bar{4}3m$ structure.

Introduction

Tricyclo[3, 3, 1, $1^{3,7}$]decane, or adamantane, $C_{10}H_{16}$, is a hydrocarbon whose molecules have a highly symmetrical (T_d) cage-like structure. A solid at room temperature, adamantane has the remarkably high melting point of 270 °C, measured in a sealed tube. The compound sublimes easily even at room temperature.

The crystal structure of adamantane has been studied at room temperature by Nowacki (1945) and by Giacomello & Illuminati (1945) using powder X-ray data. The structure is face centered cubic, and the unit cell contains four molecules. The good agreement obtained with the available X-ray data led these authors to conclude that the structure belongs to the non-centrosymmetric space group $F\bar{4}3m$ (T_d^2). Indeed, the structure proposed by them is the only chemically reasonable one assuming an ordered arrangement of the molecules.

In a recent low temperature heat capacity study Chang & Westrum (1960) discovered that adamantane undergoes a phase transition at 208·62 °K accompanied by an entropy change of 3·87 cal.deg^{-1}. mole^{-1}. The high value of the entropy change suggested the possibility of some previously undetected molecular disorder in the room temperature phase. At about the same time a muclear magnetic resonance study of solid adamantane by McCall & Douglass (1960) indicated that the room temperature structure is disordered.

As part of a series of single-crystal X-ray studies of compounds exhibiting phase transitions we have undertaken a determination of the structure of adamantane below the transition point. In view of the indications of disorder above the transition point we decided to redetermine the room temperature structure also, using single-crystal X-ray data.

Low-temperature structure

Satisfactory crystals of the room-temperature modification were found to have grown on the walls of a storage vial, *i.e.* by slow sublimation in air at room temperature. Owing to the softness of the material some difficulty was encountered in removing the crystals from the wall without distorting them. Touching the outside of the glass wall with the tip of a hot soldering pencil, causing the crystals to fall off, was found to be a satisfactory way of obtaining undistorted specimens 0·3 to 0·5 mm in size. These were mounted in sealed glass capillaries for X-ray examination.

The low-temperature form was obtained by cooling the crystal, mounted on a precession camera, in a stream of cold nitrogen gas. Diffraction patterns taken above and below the transition temperature showed