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The Crystal Structure of Pyridazino[4,5-*d*]pyridazine*

BY C. SABELLI
Centro Nazionale di Cristallografia del C.N.R., Istituto di Mineralogia dell'Università di Firenze, Italy

AND P. TANGOCCI AND P. F. ZANAZZI
Istituto di Mineralogia dell'Università di Perugia, Italy

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The crystal structure of pyridazino[4,5-*d*]pyridazine, $C_6H_4N_4$, has been determined by a three-dimensional Patterson synthesis and on the basis of the strongest reflexion $10\bar{2}$, and refined by iterative least-squares calculations, to an R value of 0·062. The unit-cell dimensions are $a=3{\cdot}748$, $b=7{\cdot}464$, $c=10{\cdot}392$ Å and $\beta=95{\cdot}62°$; the cell contains two molecules and the space group is $P2_1/c$. Crystals tested for X-ray work were found to be twinned with an (001) twinning plane. The thermal motion was interpreted in terms of rigid-body vibrations, and small corrections were made in the bond lengths to correct errors resulting from rotational oscillations. The unusually high melting point of the compound was related to packing.

Introduction

The X-ray work on $C_6H_4N_4$, pyridazino [4,5-*d*] pyridazine or 2,3,6,7-tetrazanaphthalene, was undertaken in order to contribute to the knowledge of crystal and molecular structures of heterocyclic compounds with rings containing nitrogen atoms. This compound, a heterocyclic ring of very high symmetry, has been recently synthesized at the Istituto di Chimica Organica of the Florence University (Adembri, De Sio, Nesi & Scotton, 1967). The crystals of pyridazino[4,5-*d*]-pyridazine are yellow needles, soluble in water; they melt with decomposition at about 290°. The very high melting point has been tentatively explained from an analysis of the packing of the molecules in the crystal.

Experimental

The sample of $C_6H_4N_4$ used in this investigation was kindly supplied by Dr Nesi. Some well-formed crystals, suitable for X-ray study, were obtained by recrystallization from a methanol solution.

The unit cell of pyridazino[4,5-*d*]pyridazine is monoclinic and its dimensions were determined from basal Weissenberg photographs. The cell parameters were refined by a least-squares method from the d values of high Bragg-angle reflexions, measured on $h0l$, $hk0$ and $0kl$ Weissenberg photographs taken at room temperature and calibrated with Ag powder.

The results are: $a=3{\cdot}748\pm0{\cdot}001$, $b=7{\cdot}464\pm0{\cdot}002$, $c=10{\cdot}392\pm0{\cdot}002$Å; $\beta=95{\cdot}62°\pm0{\cdot}03°$.

From the systematic absences $h0l$ with $l=2n+1$ and $0k0$ with $k=2n+1$ the space group was uniquely determined as $P2_1/c$. Assuming two molecules in the unit cell, the calculated density is 1·516 g.cm^{-3}; the experimental density, measured by flotation in a mixture of carbon tetrachloride and chloroform is 1·53 g.cm^{-3}.

For the structural study a fragment from a thin needle elongated in the [100] direction was chosen and the reflexions from $0kl$ to $3kl$ and from $h0l$ to $h3l$ were collected with an equi-inclination integrating Weissenberg apparatus, with the use of the multiple-film technique and Cu $K\alpha$ radiation. Intensities were measured with a microdensitometer and converted to F^2 values by correction for Lorentz and polarization factors. Absorption correction was not considered necessary, owing to the small absorption coefficient (μ=8·7 cm^{-1} for Cu $K\alpha$) of the crystal; 613 independent reflexions were recorded, of which 445 were in the measurable range. An intensity just below the threshold value was given to the unobserved diffraction effects and they were omitted from the first calculations. To obtain a unique set of data, the scaling of F^2 from different layers was carried out by the correlation of the common reflexions and application of graphical methods in order to determine the best relative scale factors.

Twinning

Pyridazino[4,5-*d*]pyridazine crystals tested for X-ray work were found to be twinned, with an (001) twinning plane. The two twin components have antiparallel b^* and c^* reciprocal space axes, the a^* axes making an angle of 11° 14′. Because of this twinning the diffraction effects from the A and B components are superposed on the hkl reciprocal lattice layers when h is even. This feature does not affect the intensities on the $0kl$ layer, because diffraction effects with indices $0kl$ of the A component are superposed on the reflexions with indices $0\bar{k}\bar{l}$ of the B component; however, for the $2kl$ and $4kl$ layers each experimental intensity is the sum

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of two reflexions with different indices, since *hkl* reflexions of the *A* component of the twin are superposed on $h\bar{k}l'$ from the *B* component. There is a simple relationship between the values of the *l* and *l'* indices of the superposed reflexions as a result of the geometry of the reciprocal lattice: *l'* is $-(l+1)$ for the 2*kl* reflexions, and $-(l+2)$ for 4*kl* reflexions. Therefore it was necessary to apply the appropriate correction to these intensities by solving the equations:

$$I_{hkl}=I^{A}_{hkl}+I^{B}_{h\bar{k}l'}$$
$$I_{hkl'}=I^{A}_{hkl'}+I^{B}_{h\bar{k}l}\,,$$

where *I* is the composite intensity measured on the photographs and I^A and I^B are the intensities of two superposed reflexions. Solution is possible if the volumes of the twin components are not equal and the ratio of the intensities of corresponding reflexions from the *A* and *B* components is known. This ratio was evaluated from the intensities of reflexions of the 1*kl* and 3*kl* layers which are not affected by superposition.

Structure determination and refinement

Since the content of the unit cell is $Z=2$, the inversion centre of the pyridazino[4,5-*d*]pyridazine molecule must occupy the special position $\bar{1}$ of the space group. Furthermore, the observation that the $10\bar{2}$ reflexion is by far the strongest one on the photographs gives a reasonably clear indication that the molecule lies approximately in the $(10\bar{2})$ plane. With the unique set of F^2 data, obtained after application of the correction for twinning to the 2*kl* and 4*kl* reflexions, a three-dimensional Patterson synthesis was computed, from which the orientation of the molecule was easily found. The atomic positions were better determined by successive three-dimensional Fourier syntheses, until the value of the *R* index, defined as $\Sigma\,||F_o|-|F_c||/\Sigma\,|F_o|$, was 0·23.

At this stage first least-squares refinement was carried out with a program written by Albano, Bellon, Pompa & Scatturin (1963) for the IBM 1620 computer, with the use of the block-diagonal approximation and individual isotropic thermal parameters. The weighing scheme suggested by Cruickshank (1961*b*), $\sqrt{w}=1/(a+F_o+cF_o^2)$, with $a=2\,F_{\min}$ and $c=2/F_{\max}$, was applied to the structure factors of observed reflexions. After three cycles, the *R* index dropped to the value 0·13. At this stage the refinement* was continued with the full-matrix least-squares program of Busing & Levy, adapted for the IBM 7090 computer by Stewart (1964).

For the observed structure factors the weighting scheme of Hughes (1941) was used, with $\sqrt{w}=1$ for reflexions with $F_o \leq 4\,F_{\min}$; $\sqrt{w}=4\,F_{\min}/F_o$ for $F_o > 4\,F_{\min}$. In this new series of calculations the unobserved reflexions were included (with $\sqrt{w}=1$) only if the calculated value of *F* exceeded the threshold of observation. After one isotropic and two anisotropic cycles, a three-dimensional difference synthesis was computed, from which the hydrogen atoms were located. A last cycle of refinement was then carried out for all atoms. Thermal parameters of hydrogen atoms were set equal to the isotropic *B*'s of the carbon atoms to which they are bound, and were left unchanged during the computations. This last cycle reduced the *R* value to 0·062. The positional and thermal parameters, as well as their standard deviations, are listed in Table 1 and Table 2 respectively. The observed and calculated structure factors are given in Table 3. The atomic scattering factors from *International Tables for X-ray Crystallography* (1962) for N, C and H were used.

Table 1. *Fractional atomic coordinates with their standard deviations*

	x	*y*	*z*
N(1)	0·1453 (8)	0·3036 (3)	0·0917 (3)
N(2)	0·2805 (7)	0·1818 (4)	0·1834 (2)
C(1)	−0·0196 (8)	0·2453 (4)	−0·0170 (3)
C(2)	0·2410 (7)	0·0102 (4)	0·1624 (3)
C(3)	−0·0675 (7)	0·0609 (4)	−0·0463 (2)
H(1)	−0·088 (11)	0·346 (6)	−0·070 (4)
H(2)	0·366 (11)	−0·064 (6)	0·222 (4)

Results and discussion

The structure of pyridazino[4,5-*d*]pyridazine projected along the *a*, *b* and *c* axes is shown in Figs. 1, 2 and 3.

The molecule is planar within the limits of experimental error, the equation of the mean square plane through the nitrogen and carbon atoms being

$$3{\cdot}427x-0{\cdot}095y-5{\cdot}118z=0\,,$$

where *x*, *y* and *z* are the fractional atomic coordinates referred to the monoclinic cell axes. The displacements Δ of the atoms from the plane are listed in Table 4.

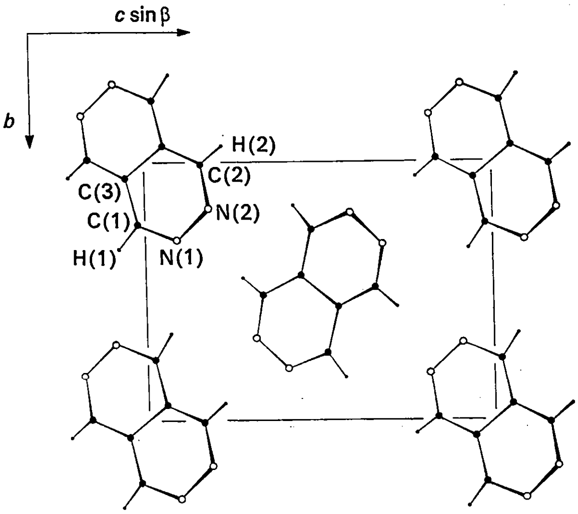

Fig. 1. Projection of the structure along the *a* axis.

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* The calculations were performed with the IBM 7090 computer of the Centro Nazionale di Calcolo Elettronico of the Pisa University.

Table 2. *Thermal parameters and standard deviations*

For non-hydrogen atoms the β_{ij} coefficients of the expression:

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

are listed; for hydrogen atoms the isotropic B's (Å^2) are given.

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
N(1)	0·0936 (22)	0·0117 (4)	0·0093 (3)	−0·0030 (8)	0·0031 (6)	−0·0010 (3)
N(2)	0·0877 (22)	0·0155 (5)	0·0079 (2)	−0·0051 (8)	−0·0004 (6)	−0·0009 (3)
C(1)	0·0766 (22)	0·0102 (5)	0·0088 (3)	0·0027 (9)	0·0033 (6)	0·0015 (3)
C(2)	0·0687 (23)	0·0156 (6)	0·0067 (2)	0·0001 (9)	−0·0005 (6)	0·0009 (3)
C(3)	0·0533 (17)	0·0106 (4)	0·0066 (2)	0·0015 (7)	0·0025 (5)	0·0007 (3)
	B					
H(1)	3·82					
H(2)	3·82					

Table 3. *Observed and calculated structure factors* (× 10)

The calculated factors are referred to the cell whose origin is displaced by $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$. The asterisk designates the unobserved reflexions.

H	K	L	FO	FC
0	0	2	169	196
		4	23	-23
		6	102	105
		8	88	-89
		10	15 *	0
		12	26	26
0	1	1	193 E	262
		2	205 E	259
		3	125	-137
		4	143	-143
		5	145	145
		6	60	-52
		7	24	21
		8	83	-84
		9	89	-89
		10	74	-72
		11	17	-18
		12	11 *	15
		13	8	-8
0	2	0	167	-179
		1	47	48
		2	113	-119
		3	175	-188
		4	43	-39
		5	139	-129
		6	24	21
		7	50	47
		8	29	-29
		9	25	-24
		10	86	-91
		11	13 *	-2
		12	11 *	-14
		13	7	9
0	3	1	171	169
		2	125	-125
		3	22	22
		4	67	-61
		5	129	-124
		6	27	-22
		7	14 *	-1
		8	29	28
		9	15 *	-16
		10	23	23
		11	12 *	-9
		12	9 *	11
0	4	0	182	185
		1	67	-55
		2	75	67
		3	69	70
		4	14 *	9
		5	26	-20
		6	73	70
		7	99	-106
		8	24	19
		9	15 *	-12
		10	13 *	-6
		11	11 *	-3
		12	6 *	23
0	5	1	28	-27
		2	65	-66
		3	102	-99
		4	56	-54
		5	106	106
		6	85	-83
		7	50	46
		8	31	-34
		9	41	-42
		10	17	-18
		11	8 *	8
0	6	0	29	26
		1	15 *	-6
		2	106	-111
		3	89	-88
		4	89	-90
		5	72	-70
		6	15 *	9
		7	23	20
		8	34	-36
		9	11 *	-5
		10	9 *	6
0	7	1	15 *	-6
		2	61	64
		3	53	-57
		4	24	-23
		5	26	-26
		6	15	14
		7	13 *	12
		8	10 *	5
0	8	0	36	-37
		1	24	27
		2	13 *	1
		3	15 *	12
		4	24	22
		5	11 *	-5
		6	53	44
0	9	1	17	-16
		2	30	-27
		3	16	-10
		4	15	-14
1	0	0	356 E	-431
		2	108	106
		-2	518 E	-819
		4	145	-158
		-4	21	20
		6	72	73
		-6	44	-42
		8	36	34
		-8	31	-31
		10	46	-46
		-10	63	62
		12	28	23
		-12	13 *	-12
1	1	0	257	-269
		1	173	121
		-1	257	-295
		2	91	84
		-2	104	97
		3	111	-103
		-3	63	-56
		4	103	96
		-4	89	90
		5	90	-87
		-5	45	45
		6	70	70
		-6	98	-93
		7	95	100
		-7	95	-94
		8	108	111
		-8	29	-27
		9	43	42
		-9	18 *	22
		10	16 *	-8
		-10	67	-67
		11	14 *	4
		-11	58	55
		12	10 *	-8
		-12	37	-31
1	2	0	108	107
		1	112	110
		-1	29	-27
		2	56	51
		-2	125	126
		3	194	195
		-3	17	17
		4	12 *	-7
		-4	67	63
		5	45	-45
		-5	153	-151
		6	15 *	2
		-6	25	17
		7	16 *	10
		-7	50	-45
		8	105	110
		-8	18 *	-16
		9	18 *	17
		-9	19 *	20
		10	39	42
		-10	41	42
		11	15 *	-15
		-11	16 *	-19
		12	9 *	-8
		-12	57	53
1	3	0	113	110
		1	74	-73
		-1	141	-137
		2	74	72
		-2	41	-37
		3	135	129
		-3	110	-108
		4	46	36
		-4	78	-74
		5	36	29
		-5	29	24
		6	27	-20
		-6	43	-39
		7	16 *	-2
1	3	-7	68	63
		8	28	-32
		-8	17 *	-7
		9	27	28
		-9	16 *	-5
		10	14 *	-12
		-10	22	21
		11	36	-32
		-11	15 *	20
		12	7 *	-20
		-12	10 *	13
1	4	0	105	-98
		1	31	-34
		-1	38	27
		2	14 *	2
		-2	169	-138
		3	30	-27
		-3	46	-37
		4	66	-66
		-4	26	-24
		5	122	127
		-5	52	51
		6	52	-46
		-6	19	-22
		7	31	33
		-7	48	-47
		8	16 *	12
		-8	51	-47
		9	15 *	0
		-9	57	-59
		10	28	-24
		-10	14 *	0
		11	9 *	-10
		-11	11 *	-4
		-12	7 *	-2
1	5	0	53	56
		1	111	107
		-1	15 *	-10
		2	44	44
		-2	28	-25
		3	66	-65
		-3	62	58
		4	87	88
		-4	50	-53
		5	96	-91
		-5	47	44
		6	48	51
		-6	55	-53
		7	45	47
		-7	89	-89
		8	15 *	17
		-8	57	-58
		9	13 *	4
		-9	14 *	-7
		10	25	23
		-10	21	-20
		-11	22	21
1	6	0	64	66
		1	60	60
		-1	16 *	4
		2	118	122
		-2	16 *	-9
		3	92	93
		-3	18 *	-15
		4	17 *	-3
		-4	108	112
		5	16 *	-10
		-5	83	-83
		6	34	33
		-6	39	40
		7	14 *	-6
		-7	35	-34
		8	13 *	11
		-8	14 *	-3
		9	26	17
		-9	6	13
		-10	24	24
1	7	0	61	-64
		1	47	50
		-1	16 *	-1
		2	16 *	11
		-2	29	31
		3	41	41
		-3	16 *	16
		4	15 *	2
		-4	31	35
		5	14 *	-8
		-5	45	47
1	7	6	17	-16
		-6	16 *	-19
		7	11 *	-14
		-7	12 *	8
		8	19	18
		-8	19	17
		-9	6 *	-10
1	8	0	14 *	10
		1	16 *	-20
		-1	14 *	-16
		2	15 *	-20
		-2	30	30
		3	13 *	7
		-3	27	27
		4	46	-37
		-4	13 *	-6
		5	11 *	-7
		-5	12 *	3
		6	52	-51
		-6	22	-19
		-7	7 *	-1
1	9	0	26	23
		1	11 *	9
		-1	24	16
		2	17	16
		-2	9 *	-9
		-3	15	14
2	0	0	68	-65
		2	110	101
		-2	360	325
		4	11 *	-7
		-4	275	274
		6	62	-62
		-6	28	-26
		8	43	44
		-8	44	43
		10	15	-9
		-10	11 *	-4
		-12	34	-32
2	1	0	10	9
		1	23	13
		-1	17	-16
		2	99	-93
		-2	135	121
		3	107	101
		-3	174	154
		4	42	-40
		-4	74	-71
		5	67	-67
		-5	10 *	-8
		6	103	-107
		-6	12 *	-1
		7	60	-63
		-7	14	2
		8	13 *	-15
		-8	42	43
		9	11 *	-2
		-9	40	42
		10	17	17
		-10	20	20
		11	25	-19
		-11	31	-29
		-12	40	39
2	2	0	41	-35
		1	156	-146
		-1	26	-26
		2	12	-10
		-2	43	-51
		3	11 *	3
		-3	9 *	0
		4	12 *	11
		-4	53	-50
		5	11 *	10
		-5	20	14
		6	82	-88
		-6	32	-30
		7	33	-29
		-7	77	82
		8	64	-68
		-8	12 *	-4
		9	13	15
		-9	12 *	10
		10	9 *	9
		-10	11 *	4
		11	6 *	-4
		-11	9 *	-2
		-12	33	-34
2	3	0	59	-59
		1	75	-69
		-1	64	65
		2	38	-35
		-2	52	-50
		3	52	-47
		-3	78	73
		4	11 *	1
		-4	33	31
		5	11	15
		-5	44	43
		6	26	29
		-6	37	36
		7	34	-36
		-7	29	-28
		8	13	13
		-8	26	23
		9	25	23
		-9	18	-20
		10	19	17
		-10	10 *	0
		-11	8 *	-1
2	4	0	11 *	2
		1	36	36
		-1	11 *	-4
		2	37	36
		-2	86	84
		3	90	-94
		-3	11 *	3
		4	61	60
		-4	66	68
		5	53	-54
		-5	14	13
		6	12 *	-8
		-6	12 *	6
		7	11 *	3
		-7	14	-15
		8	11	15
		-8	22	23
		9	8 *	1
		-9	40	41
		10	22	21
		-10	11	21
		-11	22	25
2	5	0	31	-32
		1	12 *	3
		-1	61	-61
		2	66	-66
		-2	28	-29
		3	95	96
		-3	15	14
		4	54	-58
		-4	20	28
		5	24	-26
		-5	52	-54
		6	12 *	-15
		-6	35	37
		7	16	-20
		-7	11 *	-2
		8	24	-25
		-8	39	40
		9	18	16
		-9	50	49
		-10	33	32
2	6	0	98	-105
		1	75	-78
		-1	17	-26
		2	16	-15
		-2	23	-23
		3	13 *	-13
		-3	12 *	-6
		4	17	-16
		-4	15	-17
		5	11	15
		-5	22	22
		6	25	-25
		-6	71	-75
		7	21	-19
		-7	55	55
		8	32	28
		-8	8 *	-9
		-9	6 *	11
2	7	0	11 *	7
		1	39	-42
		-1	30	-34
		2	16	-16
		-2	34	37
		3	10 *	0
2	7	-3	10 *	1
		4	21	19
		-4	34	-35
		5	15	14
		-5	21	-21
		6	14	-15
		-6	8 *	-8
		-7	25	-27
2	8	0	14	12
		1	8 *	-5
		-1	21	20
		2	28	25
		-2	16	-16
		3	7 *	3
		-3	8 *	3
		4	47	47
		-4	16	-17
		-5	15	-17
3	0	0	34	-32
		2	40	-35
		-2	9 *	-2
		4	53	54
		-4	170	-176
		6	15	-17
		-6	78	-81
		-10	24	-24
3	1	0	64	54
		1	69	-62
		-1	18	14
		2	26	24
		-2	33	-27
		3	22	20
		-3	36	-30
		4	61	66
		-4	36	-34
		5	58	62
		-5	65	-67
		6	29	31
		-6	29	28
		7	8 *	8
		-7	12	11
		8	17	-18
		-8	15	-16
		9	14	12
		-9	8 *	-12
		-10	20	-18
3	2	0	16	15
		1	31	26
		-1	73	71
		2	9 *	-8
		-2	19	18
		3	13	-13
		-3	9 *	1
		4	47	49
		-4	14	14
		5	25	25
		-5	9 *	4
		6	63	70
		-6	19	18
		7	10	-7
		-7	16	-21
		8	7 *	-1
		-8	9	15
		-9	35	-37
		-10	6 *	-2
3	3	0	26	27
		1	37	37
		-1	22	22
		2	11	11
		-2	36	36
		3	13	-13
		-3	37	-39
		4	13	-15
		-4	16	15
		5	22	26
		-5	34	-36
		6	10	-12
		-6	17	-17
		7	7 *	-5
		-7	11	-11
		8	7	-11
		-8	18	-19
		-9	15	15
		-10	5 *	-12
3	4	0	9 *	-10
		1	44	47
		-1	15	-17
3	4	2	45	-47
		-2	9	-10
		3	49	54
		-3	10 *	10
		4	9 *	-3
		-4	49	-53
		5	8 *	0
		-5	9 *	-10
		6	7 *	-2
		-6	25	-25
		7	6 *	3
		-7	9 *	-4
		-8	7 *	-3
		-9	5 *	-4
3	5	0	34	39
		1	58	-60
		-1	17	24
		2	49	49
		-2	18	20
		3	8 *	-2
		-3	19	19
		4	16	14
		-4	9 *	8
		5	33	26
		-5	8 *	-3
		6	18	19
		-6	20	-21
		-7	30	32
		-8	21	-24
3	6	0	26	28
		1	27	26
		-1	46	44
		2	7 *	2
		-2	62	63
		3	16	-12
		-3	8 *	9
		4	26	24
		-4	7 *	5
		-6	24	25
3	7	0	17	17
		-1	30	32
		-2	12	-13
		-3	17	18
4	0	0	13 *	33
		2	12 *	-25
		-2	13 *	6
		4	10 *	-7
		-4	30	26
		-6	79	82
		-8	18	21
4	1	0	18	17
		1	9 *	4
		-1	24	24
		2	31	-29
		-2	24	-22
		3	46	-42
		-3	9 *	-7
		4	33	-29
		-4	19	18
		5	14	-14
		-5	31	31
		6	11	9
		-6	6 *	6
		-7	29	25
4	2	0	7 *	2
		1	7 *	4
		-1	28	-27
		2	24	-20
		-2	14	-11
		3	20	-14
		-3	28	-27
		4	62	-50
		-4	7 *	-5
		-5	6 *	1
		-6	6 *	0
		-7	6 *	-1
4	3	0	11	-13
		1	6 *	6
		-1	18	-20
		2	6 *	2
		-2	15	-18
		3	15	-13
		-3	6 *	-3
		-4	16	-17
		-5	20	21
		-6	5 *	-3
		-7	15	15

Table 4. *Deviations of atoms from least-squares plane* (Å)

	Δ
N(1)	0·000
N(2)	0·005
C(1)	−0·003
C(2)	−0·006
C(3)	0·000
H(1)	0·02
H(2)	0·02

Since the molecule is centrosymmetric, and on the assumption that the internal vibration is fairly small (Higgs, 1955), the thermal motion has been analysed in terms of rigid-body vibrations, according to the method proposed by Cruickshank (1956); the calculations were carried out with a program written for the IBM 1620 computer by the authors. The anisotropic temperature factors β_{ij} in Table 2 were transformed into U_{ij} referred to the molecular axes, chosen as follows: the origin of the axes to lie at the centre of symmetry; the

X axis to pass between atoms N(1) and N(2); the *Y* axis to be perpendicular to *X* in the molecule plane; *Z* to be perpendicular to both the *X* and *Y* axes. The direction cosines of the molecular axes referred to the crystallographic axes are:

X	0·2748	0·7537	0·5672
Y	0·2988	−0·6542	0·6623
Z	0·9142	−0·0127	−0·4925

The values of the six independent U_{ij}'s for each atom are shown in Table 5 in the columns headed 'obs.' From the **U** tensors, the **T** and **ω** tensors were computed by Cruickshank's least-squares method, and the values obtained are given in Table 6. These values are fairly similar to those found for naphthalene (Cruickshank, 1957), except that the translational tensor is smaller, as was expected from the higher melting point of pyridazino[4,5-*d*]pyridazine, which indicates a stronger molec-

Table 5. *Observed and calculated* U_{ij} (10^{-2}Å^2)

	U_{11}		U_{22}		U_{33}		U_{12}		U_{13}		U_{23}	
	obs.	calc.	obs.	calc.	obs.	calc.	obs.	calc.	obs.	calc.	obs.	calc.
N(1)	3·69	3·78	4·99	5·01	6·26	6·30	0·98	1·01	0·31	0·30	0·60	0·61
N(2)	3·71	3·77	4·89	4·99	6·35	6·30	−0·13	−0·18	−0·08	−0·02	0·63	0·63
C(1)	4·46	4·25	3·43	3·51	5·14	5·09	1·16	1·01	0·29	0·29	0·20	0·20
C(2)	4·33	4·24	3·58	3·50	5·07	5·11	−0·38	−0·20	0·00	−0·04	0·23	0·23
C(3)	3·62	3·77	3·08	2·93	3·60	3·60	0·41	0·40	0·15	0·13	0·07	0·06

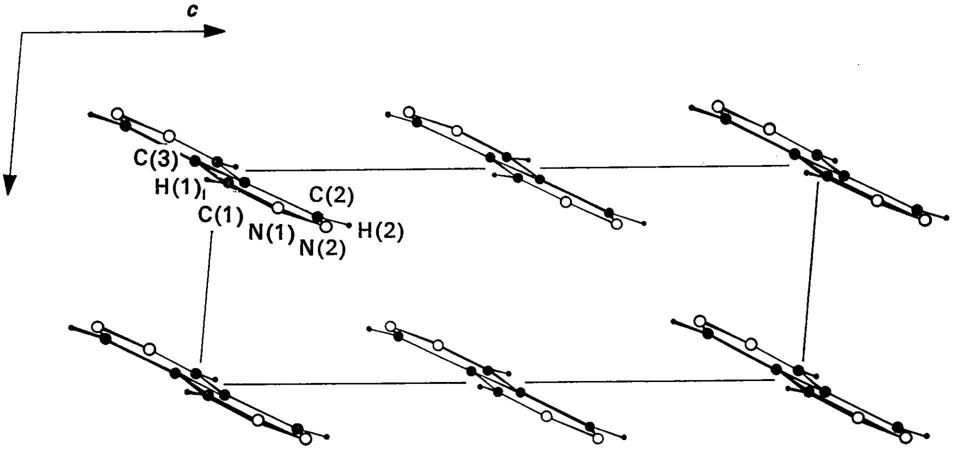

Fig. 2. Projection of the structure along the *b* axis.

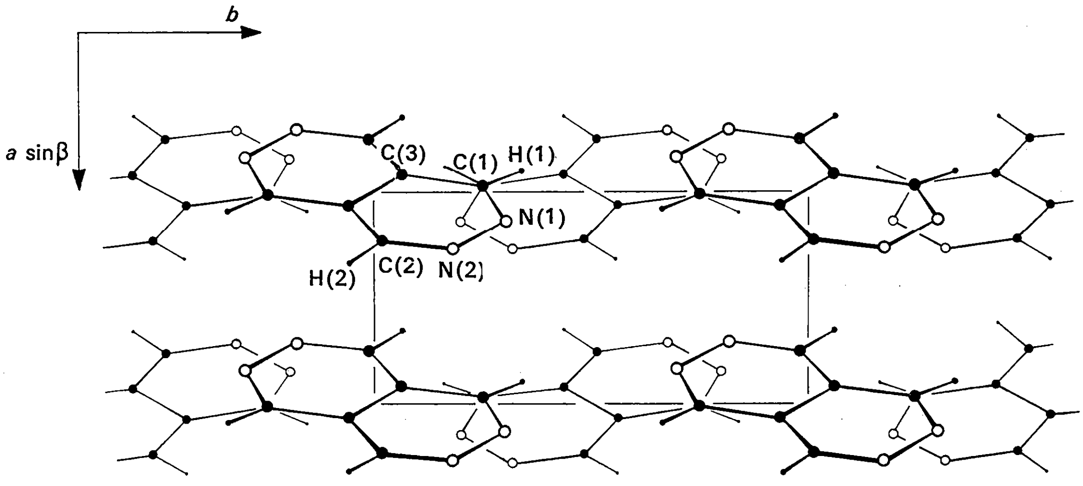

Fig. 3. Projection of the structure along the *c* axis.

ular association in the crystal. From the **T** and **ω** tensors, the **U** tensor for each atom was calculated. The values of U_{ij} so derived are listed in Table 5 in the columns headed 'calc.'

Table 6. *Values of* T_{ij} (10^{-2}Å^2) *and* ω_{ij} (deg.)

$$\mathbf{T} = \begin{bmatrix} 3{\cdot}60 & 0{\cdot}40 & 0{\cdot}14 \\ & 2{\cdot}93 & 0{\cdot}06 \\ & & 3{\cdot}33 \end{bmatrix}$$

$$\boldsymbol{\omega} = \begin{bmatrix} 18{\cdot}84 & -0{\cdot}20 & 0{\cdot}23 \\ & 15{\cdot}46 & -3{\cdot}20 \\ & & 11{\cdot}85 \end{bmatrix}$$

The root-mean-square amplitudes of translational and rotational vibrations in the three principal molecular directions, computed from the diagonal elements of the **T** and **ω** tensors, are 0·19, 0·17, 0·18 Å and 4·3, 3·9, 3·4° respectively. These amplitudes are not significantly different from each other, and it may be concluded that the molecular motion is essentially isotropic.

The interatomic distances and angles were then corrected for the angular oscillation according to the method of Cruickshank (1961*a*). The correction in bond lengths is small (maximum 7.10^{-3} Å); the angles are modified only negligibly (up to 5.10^{-2} degrees). In Table 7 the uncorrected and corrected values for distances are listed. The values for bond angles are given in Table 8. The dimensions of the pyridazino[4,5-*d*]-pyridazine molecule are also shown in Fig. 4. Chemically equivalent bonds and angles are all equal in value, within the limits of experimental error.

Table 7. *Bond lengths* (Å)

	Distance* Uncorrected	Distance* Corrected†
N(1)–N(2)	1·377	1·382
N(2)–C(2)	1·305	1·310
N(1)–C(1)	1·308	1·314
C(1)–C(3)	1·417	1·423
C(2)–C(3)	1·417	1·423
C(3)–C(3′)	1·383	1·388
C(1)–H(1)	0·95	
C(2)–H(2)	0·88	

* Estimated standard deviations are: N–N, 0·004; C–N, 0·004; C–C, 0·004; C–H, 0·04 Å.

† The shape parameter (q^2) used in calculating bond length corrections was 0·12.

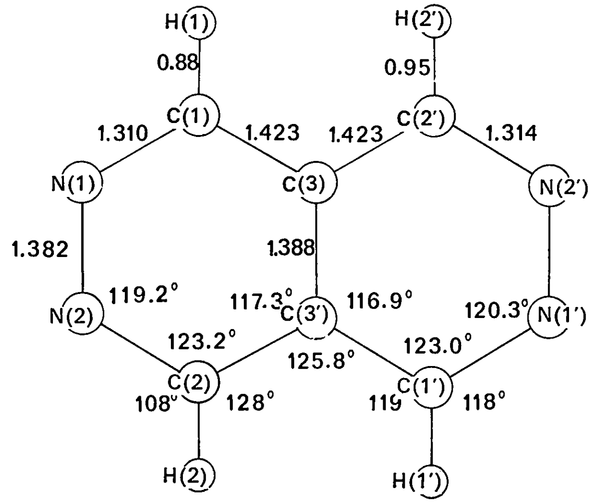

Fig. 4. The dimensions of pyridazino[4,5-*d*]pyridazine molecule.

Table 8. *Bond angles with standard deviations*

N(1)–N(2)–C(2)	119·2 ± 0·2°
N(2)–N(1)–C(1)	120·3 ± 0·2
N(2)–C(2)–C(3′)	123·2 ± 0·3
N(1)–C(1)–C(3)	123·0 ± 0·3
C(2)–C(3′)–C(3)	117·3 ± 0·2
C(1)–C(3)–C(3′)	116·9 ± 0·2
C(1)–C(3)–C(2′)	125·8 ± 0·2
N(2)–C(2)–H(2)	108 ± 3°
H(2)–C(2)–C(3′)	128 ± 3
N(1)–C(1)–H(1)	118 ± 3
H(1)–C(1)–C(3)	119 ± 3

It is interesting to compare our results with those of Bertinotti, Giacomello & Liquori (1956) for *s*-tetrazine: in pyridazino[4,5-*d*]pyridazine there is a shortening in the C–N bond length and a lengthening of the N–N distance; we found 1·312 and 1·382 Å respectively, as against the values 1·334 and 1·321 Å of *s*-tetrazine. This fact can be explained by taking into account the different contributions of 'naphthalene-like' mesomeric formulae to the molecular structure.

While the C(1)–C(3) bond, 1·423 Å long, is comparable with the homologous distance in naphthalene, 1·425 Å (Cruickshank, 1957), the C(3)–C(3′) bond length (1·388 Å) is less than the corresponding distance in naphthalene (1·410 Å). No correction for riding motion was applied to the locations of the hydrogen atoms; the C–H distances are shorter than expected, but this feature is usually observed in X-ray crystal structure determinations (Wheatley, 1953).

While Hameka & Liquori (1956) observed that in several heterocyclic compunds of nitrogen the C–N–N or the C–N angles are less than 120°, the nitrogen bond angle in pyridazino[4,5-*d*]pyridazine (119·7°), does not seem to deviate significantly from the theorical value of a pure sp^2 hybridization.

Each molecule of pyridazino[4,5-*d*]pyridazine is in contact with eight more in the crystal. The intermolecular distances below 3·5 Å are listed in Table 9. Most of the shortest intermolecular approaches are between nitrogen atoms and carbon atoms bound to nitrogen. This feature would suggest that there is an interaction between the lone pair of nitrogen atoms and C–H groups of the adjacent molecules, with a consequent special attraction between neighbouring molecules. This fact might be responsible for the unusually high melting point of the compound, because of the system of relatively strong intermolecular forces which extend through the crystal, and could also help to explain the yellow colour of pyridazino[4,5-*d*]pyridazine.

Table 9. *Shortest intermolecular distances*

Values less than 3·5 Å for contacts involving C and N atoms, and less than 3·0 Å for contacts involving C or N and H atoms.

(I)	x;	y;	z
(II)	$1+x$;	y;	z
(III)	$-x$;	$\frac{1}{2}+y$;	$\frac{1}{2}-z$
(IV)	x;	y;	$\frac{1}{2}+z$
(V)	$1-x$;	$-y$;	$-z$
(VI)	$1-x$;	$\frac{1}{2}+y$;	$\frac{1}{2}-z$
(VII)	$1-x$;	$-\frac{1}{2}+y$;	$\frac{1}{2}-z$
(VIII)	$-x$;	$1-y$;	$-z$

N(1) (I)–C(1) (II)	3·457 Å
–C(1) (VIII)	3·477
–C(2) (III)	3·425
N(2) (I)–C(1) (IV)	3·451
–C(2) (VI)	3·349
C(2) (I)–C(3) (V)	3·473
N(1) (I)–H(1) (VIII)	2·63
–H(2) (VII)	2·79
–H(2) (III)	2·94
N(2) (I)–H(2) (VI)	2·52

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The Crystal and Molecular Structure of Guanosine-5′-phosphate Trihydrate

By Wataru Murayama, Nobuya Nagashima and Yoko Shimizu

Central Research Laboratories, Ajinomoto Company, Inc., 2964 *Suzuki-cho, Kawasaki, Japan*

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The crystal structure of guanosine-5′-phosphate trihydrate has been determined by a three-dimensional sharpened Patterson function and a Fourier synthesis, and was refined by the block-diagonal matrix least-squares method to a final R index of 0·086 for non-zero intensity reflexions. The space group is $P2_12_12_1$, and the unit-cell dimensions are $a=10{\cdot}64$, $b=6{\cdot}18$ and $c=25{\cdot}58$ Å with four molecules per unit cell. Of a total of 20 hydrogen atoms in an asymmetric unit, 15 atoms are located by difference Fourier synthesis. The conformation of the guanosine-5′-phosphate molecule in the crystal is similar to that of adenosine-5′-phosphate, and differs significantly from that of the disodium salt of inosine-5′-phosphate. The conformation of purine nucleotides in the solid state is discussed in connexion with that in an aqueous solution.

Introduction

Guanosine-5′-phosphate (9-β-5′-phospho-D-ribofuranosylguanine, 5′-GMP) is one of the important ribonucleic acid constituents. To date only the hydrogen-bonded helical structure of dried GMP gel has been reported (Gellert, Lipsett & Davies, 1962). While it is of fundamental importance to determine accurate molecular dimensions for this biochemically important material, the conformation of the molecule in the solid state is also of interest.

The conformation of the ribose or deoxyribose moiety in nucleotides and nucleosides in aqueous solution has been investigated by nuclear magnetic resonance spectra (Jardetzky, 1962, 1960; Lemieux, 1961) but the results do not always coincide with those for the solid state obtained by X-ray diffraction methods. As Jardetzky points out, the conformations of the ribose or deoxyribose moiety should be affected by the crystal field.

The molecular structure of 5′-GMP established by this investigation is compared with those of analogous purine nucleotides, *i.e.* adenosine-5′-phosphate (5′-AMP; Kraut & Jensen, 1963) and the disodium salt of inosine-5′-phosphate (disodium 5′-IMP; Nagashima & Iitaka, 1968), in which the intramolecular interactions between various substituents of the ribose ring are expected to be similar. Comparison of the molecular structures of these compounds may give some information on the factors determining the stable conformation of