

The Crystal and Molecular Structure of Picolinamide

BY TSUNEHIRO TAKANO, YOSHIO SASADA AND MASAO KAKUDO

Institute of Protein Research, Osaka University, Osaka, Japan

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Picolinamide, $C_6H_6N_2O$, crystallizes in the monoclinic space group $P2_1/a$, with four molecules in a unit cell of dimensions

$$a = 16.42, \quad b = 7.11, \quad c = 5.19 \text{ \AA}, \quad \beta = 100.2^\circ.$$

The structure was solved from the two-dimensional Patterson function by a trial and error method. The atomic coordinates and thermal parameters were refined by the three-dimensional block-diagonal least-squares method.

The mean bond lengths are C–C 1.37₉, C–N 1.34₂ Å in the pyridine ring and C–C 1.51₅, C–O 1.24₁, C–N 1.33₀ Å in the amide group, with a mean standard deviation of 0.008 Å. The pyridine ring is planar within the limits of error. The angle between the plane of the pyridine ring and that of the amide group is about 19°. Non-bonded contact radii of some atoms are proposed to interpret the twisting between the amide group and the ring.

The anisotropic thermal motion of the molecule has been analysed in terms of a rigid-body approximation.

There are two sets of NH...O hydrogen bonds, the first set of length 2.96 Å joining a pair of molecules across the center of symmetry to form a dimer, and the second of length 3.01 Å joining such dimers into endless chains along the *c* axis.

Introduction

Crystal and molecular structures of amino acids and peptides have been investigated in detail by several authors because of their biochemical importance. Rather limited attention has been paid to acid amides which are closely related to amino acids or peptides and play some role in biological systems. From the viewpoint of crystal chemistry, however, it is attractive to study the variety of molecular associations by hydrogen bonding in the amide, because the amide group is a bivalent donor and bivalent acceptor at the same time.

Structural investigation of picolinamide (pyridine-2-carboxylic acid amide) has been undertaken as a part of serial studies of aromatic acid amides (Tamura, Kuwano & Sasada, 1961; Takaki, Sasada & Watanabé, 1960; Orii, Nakamura, Takaki, Sasada & Kakudo, 1963; Sasada, Takano & Kakudo, 1964; Takaki & Sasada, 1966). The present paper describes a detailed three-dimensional crystal analysis of picolinamide.

An analysis of the anisotropic thermal motion of the molecule is attempted in terms of a rigid-body approximation, in order to examine whether the approximation is applicable to such molecules connected to each other by hydrogen bonds.

Experimental

The crystals were obtained from an alcohol solution as colorless laths elongated along the *c* axis, and sometimes as plates developed on the (100) face.

The unit-cell dimensions were determined from oscillation and Weissenberg photographs taken around the *b* and *c* axes with Cu *K*α radiation ($\lambda = 1.5418 \text{ \AA}$). The crystal and physical data obtained, which are more accurate than those previously reported (Tamura, Kuwano & Sasada, 1961), are as follows:

Picolinamide, $C_6H_6N_2O$. m.p. 107–108°C

Monoclinic: $a = 16.42 \pm 0.03$, $b = 7.11 \pm 0.02$,

$c = 5.19 \pm 0.02 \text{ \AA}$, $\beta = 100.2 \pm 0.2^\circ$.

Absent spectra: $h0l$ when *h* is odd, $0k0$ when *k* is odd.

Space group: $P2_1/a$.

Density (floatation): 1.39 g.cm⁻³.

Density (calculated): 1.38 g.cm⁻³.

Four molecules per unit cell.

Total number of electrons per unit cell, $F(000) = 256$.

Linear absorption coefficient for Cu *K*α, $\mu = 8.12 \text{ cm}^{-2}$.

Intensity data were collected by the equi-inclination integrated Weissenberg procedure. Diffraction photographs were taken for layers 0–3 around the *b* axis and for layers 0–4 around the *c* axis. Cross sections of the specimens perpendicular to the axis of rotation were 0.4 × 0.3 mm for the *b*-axis rotation, and 0.4 × 0.4 mm for the *c*-axis rotation. The intensities were estimated by visual comparison with a calibrated scale, prepared with the same crystal. The multiple-film technique was applied to correlate strong and weak reflections, ranging in relative intensities from 4900 to 1. Within the limiting sphere for copper radiation, 1103 out of 1362 collectable *hkl* reflections were recorded.

Lorentz and polarization correction was applied in the usual way, but that for absorption was disregar-

ded since its effect might be negligibly small. Wilson's statistical method (1942) was employed to place the structure factors on the absolute scale.

Structure determination

Two-dimensional analysis

Two-dimensional Patterson functions, $P(UV)$ and $P(UW)$, were computed. While the interpretation of the $P(UW)$ was impossible, the distribution of peaks in the $P(UV)$ suggested that the long axis of the molecule lies approximately in the direction of [410]. Possible molecular arrangements in the (001) projection were examined with the trial model of the hydrogen-bonded dimer which was expected from structural information of the related crystals (Sasada, Takano & Kakudo, 1964; Sim, Robertson & Goodwin, 1955; Penfold & King, 1959; Takaki, Sasada & Watanabé, 1960; Orii, Nakamura, Takaki, Sasada & Kakudo, 1963). Atomic coordinates so obtained were adjusted by means of the trial and error method using structure factor maps of the $hk0$ reflections.

By successive Fourier and $(F_o - F_c)$ syntheses of the (001) projection, the discrepancy index, $R = \sum ||F_o| - |F_c|| / \sum |F_o|$, decreased to 0.25. Positional and isotropic thermal parameters were refined by the least-squares method neglecting the off-diagonal terms except for the interactions between overlapped atoms. The R value for $hk0$ became 0.23 after several cycles of the refinement. This procedure, however, deformed the molecular structure to a large extent, because of errors in some large structure factors of low indices. Further refinement without these planes reduced the R value to 0.19, leaving some deformation. At this stage it was impossible to distinguish the oxygen atom definitely from the nitrogen in the amide group and the nitrogen atom from the carbon in the ring. Therefore, the average atomic scattering factors were used for these atoms. The z coordinates were derived from the x coordinates and the estimated molecular orientation. Two possible models, in which the amide nitrogen and ring nitrogen atoms were placed at the same side about the C(7)–C(2)

bond connecting the pyridine ring with the amide group, were refined by the Fourier, $(F_o - F_c)$ and least-squares methods. After several cycles of the refinement, each model gave an R value around 0.23 for $h0l$.

Three-dimensional analysis

The three-dimensional Patterson function, $P(UVW)$, was computed. The interpretation of the Patterson function indicated that the crystal structure obtained from the two-dimensional analysis was essentially correct. The positional and isotropic thermal parameters in the two models mentioned above were refined by diagonal least-squares. Only interaction between x and z coordinates of each atom was taken into account. Some reflections of lower indices were excluded in order to avoid disturbances from the secondary extinction effect, while non-observed reflections were included by assuming that each has a value equal to one-half of the minimum $|F_o|$. After several cycles of the refinement, it was found for both of the models that one bond in the amide group was always shorter than the other. The former should be a C–O bond and the latter C–N. The assignment of the C–N and C–C bonds in the ring was done in a similar manner. Refinement was carried on until the R value dropped to 0.19. At this stage a three-dimensional $(F_o - F_c)$ synthesis was computed, in which hydrogen atoms were found at reasonable positions in the molecule. The assignment of the nitrogen atoms in the amide group and the ring was confirmed by these attached hydrogen atoms.

Further refinement was done on an IBM 7090 computer by a block-diagonal least-squares program written by T. Ashida, with anisotropic temperature factors of the form of $\exp \{ -(B_{11}h^2 + B_{22}k^2 + B_{33}l^2 + B_{12}hk + B_{23}kl + B_{13}hl) \}$. The weights for the reflections with an asterisk shown in Table 1 were dropped to 0.5 in the computation. Non-observed reflections were included with a weight of 1.0. The damping factors used for the shifts of parameters were: 0.5 for the scale factor, 0.7 for the atomic coordinates, 0.2 for the anisotropic temperature factors and 0.2 for the temperature factor of the hydrogen.

After three cycles of refinement, the R value became 0.127. The final calculated structure factors are listed in Table 1 with the observed structure factors. The atomic scattering factors for oxygen, nitrogen, carbon and hydrogen used in the calculations of structure factors were taken from *International Tables for X-ray Crystallography* (1962).

Fig. 1 shows superimposed sections of the final electron density distribution taken through the atomic centers in the picolinamide molecule. The corresponding three-dimensional difference Fourier synthesis is given in the same manner in Fig. 2. The final coordinates, estimated standard deviation and the anisotropic temperature factors of each atom are listed in Tables 2 and 3 respectively. The bond lengths and angles are shown in Table 4.

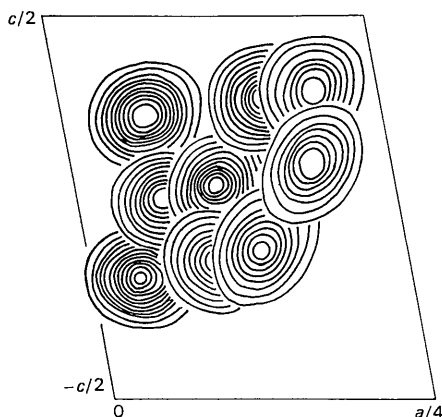


Fig. 1. Composite Fourier diagram of sections parallel to (010). Contours at intervals $1.0 \text{ e.}\text{\AA}^{-3}$, the lowest being at $1.0 \text{ e.}\text{\AA}^{-3}$.

Thermal motion

On the assumption that the internal vibration of a molecule is sufficiently small in comparison with the motion of the molecule as a rigid-body, the molecular motion can be expressed by two symmetric tensors T and ω, where T represents the anisotropic translational vibrations of the mass center and ω the anisotropic angular oscillation about the axes through the origin of the molecular axes (Cruickshank, 1956a).

For picolinamide the molecular axes were chosen as follows: OX_m passes through atoms C(2) and C(5),

OY_m is perpendicular to OX_m and in the plane of the molecule and OZ_m perpendicular to both OX_m and OY_m. The origin of axes lies at the center of symmetry. The direction cosines of the molecular axes referred to a*, b, c axes are: OX_m(0.4863, 0.8727, 0.0422), OY_m(0.4376, -0.2851, 0.8528), OZ_m(0.7546, -0.3956, -0.5194). The anisotropic temperature factors B_{ij} in Table 3 were transformed into U_{ij} referred to the molecular axes, as shown in the column headed 'obs' in Table 6.

From the U tensors, the T and ω tensors were computed by Cruickshank's least-squares method. It

Table 1. Observed and calculated structure factors

Table with multiple columns of observed and calculated structure factors for H 10FO 10FC, including values for observed (O) and calculated (C) structure factors for various reflections.

Table 1 (cont.)

H IOFO IOFC	H IOFO IOFC	H IOFO IOFC	H IOFO IOFC	H IOFO IOFC	H IOFO IOFC	H IOFO IOFC	H IOFO IOFC	H IOFO IOFC	H IOFO IOFC
-1 104 -185	10 62 -71	1 30 -33	-2 84 78	-17 57 83	-13 5c -62	1 17 21	-5 63 60	-8 0 -2	
-2 96 -101	K ₁ L ¹ , 1, 4	2 19 25	-3 32 25	K ₁ L ¹ , 3, 4	K ₁ L ¹ , 0, 5	2 16 12	-6 0 -9	-9 16 -13	
-3 41 -36	0 115 -111	3 69 67	-4 84 74	-1 119 -109	0 0 -18	3 0 10	-7 87 89	-10 0 23	
-4 0 -21	1 149 148	4 55 45	-5 0 10	-2 19 11	2 19 -1	4 26 28	-8 32 36	-11 32 -42	
-5 15 9	2 198 -226	5 27 21	-6 70 59	-3 38 -69	4 49 -42	5 45 55	-9 67 59	K ₁ L ¹ , 0, 6	
-6 32 27	3 60 45	6 0 5	-7 0 -14	-4 86 65	6 24 -52	K ₁ L ¹ , 0, 5	-10 67 62	0 0 1	
-7 43 36	4 58 -36	7 47 45	-8 0 -2	-5 0 -5	K ₁ L ¹ , 1, 5	-2 221 268	-11 29 -55	2 13 -12	
-8 71 75	5 125 -122	8 0 -17	-9 67 57	-6 94 -84	0 85 -91	-4 146 167	-12 36 38	4 21 -22	
-9 30 40	6 27 -83	9 74 76	-10 27 22	-7 55 -32	1 91 89	-6 142 -146	-13 19 -23	K ₁ L ¹ , 1, 6	
-10 58 58	7 78 -75	K ₁ L ¹ , 4, 4	-11 54 -40	-8 80 -64	2 89 -95	-8 60 -62	-14 0 15	0 0 -5	
-11 55 -52	8 20 19	0 25 -32	-12 38 -35	-9 30 50	3 0 -7	-10 75 -83	-15 33 -41	1 0 -11	
-12 9 -8	9 0 4	1 128 129	-13 26 -16	-10 0 -1	4 35 -53	K ₁ L ¹ , 1, 5	-16 5 5	2 17 15	
-13 41 -38	10 68 84	2 24 24	-14 0 -4	-11 44 32	5 34 -34	-1 27 27	-17 97 -94	3 23 28	
-14 21 25	11 22 23	3 47 48	-15 32 51	-12 42 33	6 23 -22	-2 64 67	-18 67 -63	K ₁ L ¹ , 0, 6	
K ₁ L ¹ , 7, 3	12 25 29	4 24 -27	-16 42 49	-13 67 -65	7 37 -56	-3 69 -69	-19 105 -95	-2 15 22	
-1 51 -46	K ₁ L ¹ , 2, 4	5 19 21	K ₁ L ¹ , 2, 4	-14 79 89	8 28 35	-4 60 55	-20 12 -4	-4 68 89	
-2 11 -18	0 0 -5	6 0 12	-1 38 -33	-15 0 3	K ₁ L ¹ , 2, 5	-5 96 87	-21 25 -27	-6 85 -103	
-3 33 -33	1 0 -15	7 0 17	-2 71 -58	-16 76 -93	C 78 -65	-6 128 126	-22 25 -24	-8 55 -70	
-4 80 -19	2 137 -143	8 0 -8	-3 38 -30	-17 13 20	1 89 -42	-7 46 43	-23 33 30	-10 20 26	
-5 0 -7	3 90 -79	9 42 -50	-4 127 -111	K ₁ L ¹ , 4, 4	2 75 -77	-8 74 81	-24 69 -75	K ₁ L ¹ , 1, 6	
-6 27 -27	4 81 61	K ₁ L ¹ , 0, 4	-5 43 36	-1 25 22	3 85 -78	-9 48 -51	-25 42 43	-1 0 -1	
-7 0 -5	5 120 -110	-2 246 286	-6 34 32	-2 0 11	4 16 33	-10 19 -4	-26 50 47	-2 0 18	
-8 0 -13	6 148 168	-4 67 60	-7 122 104	-3 61 -54	5 0 8	-11 56 -54	-27 57 65	-3 39 -40	
-9 28 21	7 34 36	-6 0 0	-8 0 8	-4 54 47	6 38 45	-12 22 -31	-28 32 38	-4 0 12	
-10 11 -15	8 37 22	-8 127 -111	-9 0 -23	-5 32 -30	7 0 4	-13 36 -43	-29 47 5	-5 0 -8	
-11 42 47	9 17 21	-10 62 -57	-10 0 2	-6 20 -10	8 30 31	-14 46 -66	-30 42 49	-6 0 59	
K ₁ L ¹ , 0, 4	10 15 -14	-12 119 123	-11 0 -11	-7 20 12	9 15 14	-15 23 21	-31 2 7	-7 33 79	
0 86 69	11 48 48	-14 0 -4	-12 0 -2	-8 20 17	K ₁ L ¹ , 3, 5	-16 36 -46	-32 47 -46	-8 66 59	
2 90 -78	12 18 -18	-16 0 -14	-13 37 -24	-9 0 8	0 18 -10	-1 25 -25	-33 0 4	-9 41 -25	
4 0 -14	13 19 27	-18 11 26	-14 0 18	-10 58 -63	1 0 -3	-2 18 -23	-34 71 -87	-10 12 -52	
6 84 -90	K ₁ L ¹ , 3, 4	-15 0 -1	-11 31 -27	-11 31 -27	2 66 69	-3 18 16	-35 49 -56	-11 35 -57	
8 84 -75	K ₁ L ¹ , 2, 4	-1 58 -52	-16 35 -56	-12 21 26	K ₁ L ¹ , 4, 5	-4 46 -53	-36 0 -14	-12 29 -21	

Table 2. Final atomic coordinates with their standard deviations

	x/a	y/b	z/c	$\sigma(x)$	$\sigma(y)$	$\sigma(z)$
O(9)	0.0419	0.1820	-0.1970	0.004 Å	0.004 Å	0.004 Å
N(1)	0.1669	0.4568	0.2852	0.004	0.004	0.005
N(8)	0.0686	0.1459	0.2427	0.004	0.004	0.005
C(2)	0.1168	0.4264	0.0570	0.005	0.005	0.005
C(3)	0.1031	0.5540	-0.1446	0.005	0.005	0.006
C(4)	0.1449	0.7265	-0.1053	0.006	0.006	0.006
C(5)	0.1980	0.7577	0.1245	0.006	0.006	0.007
C(6)	0.2081	0.6216	0.3149	0.006	0.006	0.006
C(7)	0.0720	0.2387	0.0241	0.005	0.005	0.005
H(10)	0.075	0.518	-0.295	0.09	0.09	0.09
H(11)	0.128	0.779	-0.227	0.07	0.07	0.07
H(12)	0.240	0.870	0.170	0.10	0.11	0.11
H(13)	0.245	0.643	0.495	0.07	0.07	0.07
H(14)	0.088	0.226	0.418	0.07	0.07	0.07
H(15)	0.039	0.037	0.171	0.11	0.12	0.11

Table 3. Final thermal parameters

The temperature factor is expressed in the form $\exp \{-(B_{11}h^2 + B_{22}k^2 + B_{33}l^2 + B_{12}hk + B_{23}kl + B_{13}hl)\}$.

	B ₁₁	B ₂₂	B ₃₃	B ₁₂	B ₂₃	B ₁₃
O(9)	0.00483	0.01665	0.02221	-0.00697	-0.01018	0.00558
N(1)	0.00301	0.01335	0.02550	-0.00268	-0.00802	0.00351
N(8)	0.00336	0.01164	0.02523	-0.00230	-0.00228	0.00451
C(2)	0.00207	0.01063	0.02599	-0.00035	-0.00504	0.00477
C(3)	0.00291	0.01260	0.03338	-0.00003	0.00208	0.00460
C(4)	0.00404	0.01365	0.04135	0.00005	0.00642	0.01191
C(5)	0.00391	0.01528	0.04731	-0.00371	-0.01650	0.01292
C(6)	0.00325	0.01885	0.03875	-0.00571	-0.01399	0.00585
C(7)	0.00288	0.01175	0.02017	-0.00171	-0.00557	0.00428

might be natural that the weights of atoms in the amide group should be decreased in the least-squares equations as shown in the last column of Table 6. The T and ω tensors and their estimated standard deviations are given in Table 5. From the result of the calculation, the natural molecular axes coincide with the principal axes OX_m , OY_m , OZ_m within experimental error.

Root-mean-square amplitudes, obtained by taking the roots of the diagonal terms of the tensors, are:

along OX_m 0.18 Å, about OX_m 4.9°
 along OY_m 0.18 Å, about OY_m 0.4°
 along OZ_m 0.16 Å, about OZ_m 2.0°.

The amplitudes of translational vibrations in the three directions are not significantly different from each other. It may be concluded that the translational motion of picolinamide is spherical, while considerable anisotropy was observed in naphthalene (Cruickshank, 1957), anthracene (Cruickshank, 1956b), azulene (Robertson, Shearer, Sim & Watson, 1962), α -pyrazinamide (Takaki, Sasada & Watanabé, 1960) and [18]-annulene (Hirshfeld & Rabinovich, 1965).

The rotational motions, on the other hand, are very characteristic. The greatest angular oscillation occurs about the long axis OX_m of the molecule and the least one about OZ_m . The feature of angular oscillation of picolinamide has some similarity to those of α -

Table 4. Bond lengths and bond angles with their standard deviations

	Without rotational correction	With rotational correction	e.s.d.
O(9)-C(7)	1.23 ₄ Å	1.24 ₁ Å	0.007 Å
N(1)-C(2)	1.33 ₅	1.33 ₅	0.007
N(1)-C(6)	1.34 ₈	1.34 ₉	0.007
N(8)-C(7)	1.32 ₂	1.33 ₀	0.007
C(2)-C(7)	1.51 ₈	1.51 ₅	0.008
C(2)-C(3)	1.37 ₃	1.37 ₂	0.008
C(3)-C(4)	1.40 ₂	1.40 ₄	0.008
C(4)-C(5)	1.36 ₅	1.36 ₇	0.008
C(5)-C(6)	1.37 ₂	1.37 ₄	0.008
O(8)-C(7)-N(8)	124.4°	125.0°	0.5°
O(8)-C(7)-C(2)	119.9	119.5	0.5
N(8)-C(7)-C(2)	115.8	115.5	0.5
C(3)-C(2)-N(1)	124.1	124.4	0.5
C(2)-C(3)-C(4)	117.2	117.1	0.5
C(3)-C(4)-C(5)	119.3	119.3	0.5
C(4)-C(5)-C(6)	119.4	119.4	0.5
C(5)-C(6)-N(1)	122.5	122.5	0.5
C(6)-N(1)-C(2)	117.4	117.3	0.4
C(7)-C(2)-N(1)	116.9	116.8	0.5
C(7)-C(2)-C(3)	119.0	118.8	0.5

pyrazinamide, naphthalene, anthracene and azulene. The broadening of the atomic peaks in the pyridine ring, as seen in Fig. 1, may be understood as a result of the angular oscillation whose center lies on the center of symmetry.

From T and ω tensors the U tensors for each atom were calculated. The values of U_{ij} so derived are listed in Table 6 in the column headed 'calc'. The vibration of carbon, nitrogen and oxygen atoms in the amide group seemed somewhat larger than expected from a rigid-body assumption.

Table 7. Intermolecular distances

Atoms at (x, y, z)	Atoms at (-x, -y, -z)	Distance
N(8)	O(9)	2.96 Å
(x, y, z)	(½-x, ½+y, 1-z)	
C(5)	N(1)	3.72
C(6)	N(1)	3.56
C(6)	N(8)	3.95
(x, y, z)	(x, y, 1+z)	
N(1)	C(3)	3.38
N(8)	O(9)	3.01
C(6)	C(4)	3.43
(x, y, z)	(x, 1+y, z)	
C(4)	O(9)	3.65
C(4)	N(8)	3.82
C(4)	C(7)	3.93
(x, y, z)	(½-x, y-½, -z)	
N(1)	C(4)	3.63
C(2)	C(5)	3.55
C(3)	C(5)	3.89
(x, y, z)	(½-x, ½+y, 1-z)	
C(5)	N(1)	3.72
C(5)	C(6)	3.99
(½-x, y-½, 1-z)	(½-x, ½+y, 1-z)	
C(5)	N(8)	3.63
(½-x, y-½, -z)	(½+x, ½-y, z)	
C(2)	C(2)	3.92
C(2)	C(3)	3.72
C(3)	C(7)	3.39
C(4)	C(7)	3.68
C(4)	C(7)	3.58
C(4)	N(8)	3.58
C(4)	O(9)	3.75

Table 5. Values of T_{ij} and ω_{ij} and e.s.d. $\sigma(T_{ij})$ and $\sigma(\omega_{ij})$

(T_{ij} and $\sigma(T_{ij})$ in 10^{-2} Å² and ω_{ij} and $\sigma(\omega_{ij})$ in deg⁻²)

$$T = \begin{bmatrix} 3.06 & 0.20 & -0.05 \\ & 3.27 & 0.89 \\ & & 2.59 \end{bmatrix} \quad \omega = \begin{bmatrix} 24.08 & -1.48 & 1.79 \\ & 0.13 & -0.03 \\ & & 4.11 \end{bmatrix}$$

$$\sigma(T) = \begin{bmatrix} 0.23 & 0.23 & 0.23 \\ & 0.42 & 0.42 \\ & & 0.50 \end{bmatrix} \quad \sigma(\omega) = \begin{bmatrix} 10.67 & 0.91 & 1.75 \\ & 0.61 & 0.58 \\ & & 0.58 \end{bmatrix}$$

Table 6. Observed and calculated values of U_{ij}

(In units of 10^{-2} Å²)

	U_{11}		U_{22}		U_{33}		U_{12}		U_{23}		U_{13}		Weight
	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.	
O(9)	3.02	3.19	5.54	3.69	5.01	3.27	-0.27	0.36	2.74	1.23	0.05	-0.08	0.5
N(1)	2.87	3.20	4.59	5.40	3.30	3.96	-0.29	-0.37	0.96	0.93	0.03	-0.14	1.0
N(8)	2.78	3.21	4.49	3.58	3.47	3.62	0.42	-0.02	1.02	1.09	0.11	-0.11	0.5
C(2)	2.65	3.06	4.24	4.81	2.00	2.61	0.10	0.23	0.23	0.86	-0.06	-0.05	1.0
C(3)	3.42	3.26	4.84	5.42	3.22	3.38	0.73	0.86	0.05	0.79	-0.11	-0.13	1.0
C(4)	4.09	3.26	6.85	7.11	3.35	3.25	1.98	1.08	0.66	0.68	-0.19	-0.12	1.0
C(5)	3.30	3.06	8.88	8.06	3.15	2.70	0.15	0.26	1.21	0.84	0.03	-0.05	1.0
C(6)	3.25	3.21	6.89	7.01	4.09	4.12	-0.92	-0.54	1.09	0.98	-0.64	-0.14	1.0
C(7)	2.77	3.06	3.96	3.79	2.76	2.59	0.05	0.21	1.08	0.87	0.11	-0.05	0.8

Table 8. Dimensions of the pyridine ring in related compounds

	N(1)-C(2) [N(1)-C(6)]	C(2)-C(3) [C(5)-C(6)]	C(3)-C(4) [C(4)-C(5)]	\angle C(2)-N(1)-C(6)	\angle N(1)-C(2)-C(3) [\angle N(1)-C(6)-C(5)]	\angle C(2)-C(3)-C(4) [\angle C(6)-C(5)-C(4)]	\angle C(3)-C(4)-C(5)
Picolinamide	1.335 Å 1.349	1.372 Å 1.374	1.404 Å 1.367	117.3°	124.4° 122.5	117.1° 119.4	119.3°
Nicotinamide	1.370 1.349	1.388 1.396	1.397 1.409	118.4	121.4 123.4	120.1 118.0	118.6
α -Pyridoin	1.334 1.349	1.380 1.405	1.384 1.384	119.0	123.1 121.1	118.6 119.0	119.2
Nicotinic acid	1.336 1.343	1.379 1.385	1.388 1.378	117.5	124.0 122.4	117.8 119.2	119.2
2,2'-Pyridil	1.349 1.359 1.321 1.343	1.403 1.371 1.401 1.377	1.343 1.414 1.403 1.413	116.5 120.5	121.7 125.4 123.7 119.2	120.1 116.1 117.7 122.4	120.1 116.6
1-Phenyl-2-(2-pyridyl)ethanedione	1.348 1.353	1.384 1.380	1.379 1.372	116.7	123.9 122.8	117.9 118.8	119.9

The bond lengths and angles corrected for the angular oscillation, with their standard deviations, are given in Table 4 (*cf.* Cruickshank, 1956*c*).

Discussion of the structure

Crystal structure

Various types of molecular arrangement connected by hydrogen bonds have been found in related crystals analysed so far (Penfold & White, 1959; Takaki, Sasada & Watanabé, 1960; Wright & King, 1954; Takaki & Sasada, 1966; Orii, Nakamura, Takaki, Sasada & Kakudo, 1963; Sasada, Takano & Kakudo, 1964). Such variation in molecular linkage is due to the fact that the amide group is a bivalent donor and a bivalent acceptor of hydrogen bonding at the same time. Furthermore, if a group attached to the amide group has an atom available for a hydrogen bond, more different types of molecular arrangement may be presumed. Polymorphism observed in the crystals of most amides may correspond to those different molecular associations (Sasada, Takano & Kakudo, 1964; Takaki & Sasada, 1966). Picolinamide crystallized in two modifications. In the first modification, for which the present analysis has been made, two molecules are joined together by a pair of NH...O hydrogen bonds of length 2.96 Å to form a dimer and such dimers are linked by the second set of NH...O hydrogen bonds of length 3.01 Å to make endless chains or bands as shown in Figs. 3 and 4. Since the dimers which are parallel to each other are slightly inclined to the direction of elongation of the band, the dimers laterally connected by hydrogen bonds to each other make as a whole pleated a band parallel to the *c* axis. The ring does not contribute to hydrogen bonding. Adjacent chains are held together by van der Waals forces. Table 7 lists the intermolecular distances less than 4.0 Å. The closest intermolecular approach except for the two sets of hydrogen bond is 3.38 Å.

While the crystal structure of the first modification resembles the crystal structures of benzamide, *m*-

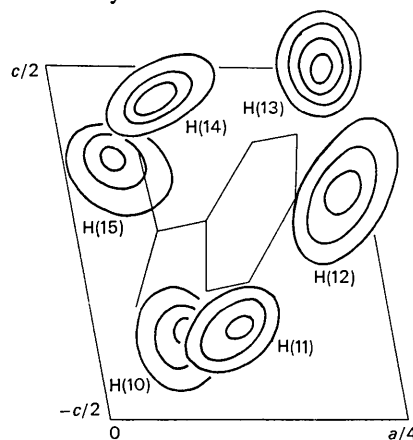


Fig. 2. Composite difference Fourier diagram of sections parallel to (010). Contours at intervals of 0.2 e.Å⁻³, the lowest being at 0.5 e.Å⁻³.

methylbenzamide and β -pyrazinamide, another modification of picolinamide, of which the unit-cell dimensions are $a=20.04$, $b=11.32$, $c=5.36$ Å, $\beta=98.6^\circ$ and the space group is $P2_1/a$, is supposed to display molecular association as seen in α -pyrazinamide crystal. In this case dimers are built up in the same way as in the first modification. In lateral linkage of such dimers, an atom in the ring plays the role of an acceptor of hydrogen bonding.

Molecular structure

Table 8 shows the dimensions of the pyridine ring obtained by X-ray analyses of several derivatives of pyridine, including picolinamide. Corresponding bond lengths and angles are of rather similar values in these related compounds, where the numberings used start from the nitrogen atoms.

It will be interesting to examine whether there is a mirror plane through the atoms N(1) and C(4) perpendicular to the molecular plane in the pyridine ring. In picolinamide, the difference between C(3)–C(4) and C(4)–C(5) might be of some significance while the differences between C(2)–C(3) and C(5)–C(6) and between N(1)–C(2) and N(1)–C(6) are not significant. Similarly, C(2)–C(3) differs significantly from C(5)–C(6) in α -pyridoin (Ashida, Hirokawa & Okaya, 1965) and C(3)–C(4) from C(4)–C(5) in one pyridine ring of 2,2'-pyridil (Hirokawa & Ashida, 1964). For the other bonds in these molecules, however, the differences between corresponding bonds are not significant. In nicotinamide, nicotinic acid, 1-phenyl-2-(2-pyridyl)-ethanedione (Ashida, Hirokawa & Okaya, 1966) and the other ring of 2,2'-pyridil, such mirror symmetry in a molecule exists within the limit of error, although the standard deviations of bond lengths for some of these are rather large. Even when the mirror symmetry in the molecule breaks down for some of these derivatives, the degree of dissymmetry is small. The same conclusion could be drawn from the comparison of the bond angles around the corresponding atoms. From these observations, it might be suggested that the substitution of the amide group into the pyridine ring

does not affect the dimensions of the ring very much. The corresponding values of the bond lengths and angles in these derivatives are averaged, in order to compare them with those obtained by microwave spectroscopy of pyridine itself. The mean values shown in Table 9 are in good agreement with those from the microwave method (Bak, Hansen & Rastrup-Andersen, 1954).

Table 9. Comparison of bond lengths and angles of the pyridine ring

	Average length and angles	Micro-wave	Theoretical
N(1)–C(2)	1.346 Å	1.340 Å	1.370 Å
C(2)–C(3)	1.386	1.390	1.380
C(3)–C(4)	1.390	1.400	1.395
\angle C(6)–N(1)–C(2)	118.0°	116.7°
N(1)–C(2)–C(3)	122.8	124.0
C(2)–C(3)–C(4)	118.8	118.6
C(3)–C(4)–C(5)	118.9	118.1

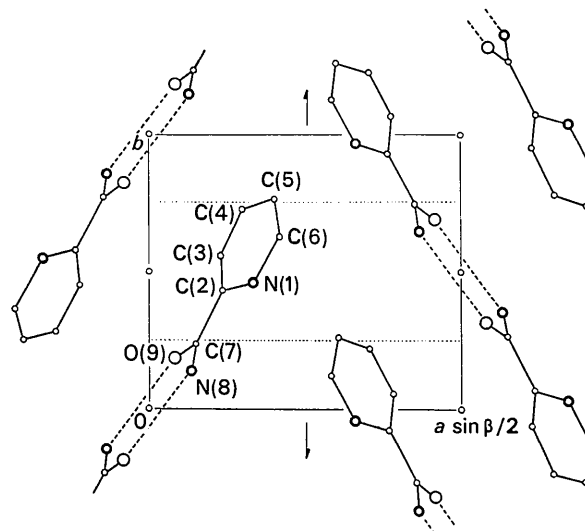


Fig. 4. Molecular arrangement in (001). Broken lines show hydrogen bonds.

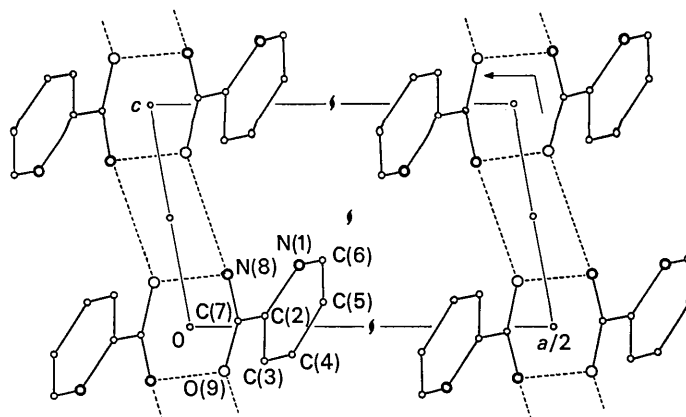


Fig. 3. Molecular arrangement in (010). Broken lines show hydrogen bonds.

They are also compatible with those theoretically derived by Longuet-Higgins and Coulson (1947) except for the C–N bond. The discrepancy between the observed and theoretical C–N bond lengths may suggest that the bond order to bond length curve for the C–N should be revised with recent data of the C–N bond.

In picolinamide molecule, the plane of the pyridine ring is well described by the equation

$$1.9077x' - y - 1.3244z' - 0.6135 = 0,$$

where $x' = x \sin \beta$ and $z' = z + x \cos \beta$, and the values of the coefficients were determined by the least-squares method. The perpendicular displacements of the atoms from the best plane through the pyridine ring are listed in Table 10. Any atom in the ring deviates by no more than 0.013 Å from the mean plane and these displacements are not significant in comparison with the values of standard deviations of the atomic coordinates. Thus it may be concluded that the pyridine ring is planar in the picolinamide molecule.

Table 10. *Displacements of atoms from an average plane through the pyridine ring*

O(9)	0.362 Å	C(4)	-0.012 Å
N(1)	-0.013	C(5)	0.004
N(8)	-0.372	C(6)	0.008
C(2)	0.006	C(7)	0.009
C(3)	0.007		

The plane of the amide group is described in the same way by the equation

$$1.9057x' - y - 0.4893z' - 0.5623 = 0.$$

The plane passing through the amide group makes an angle of 19° with the plane through the pyridine ring. This value is between the 3° found in salicylamide (Sasada, Takano & Kakudo, 1964) and the 29° in *m*-methylbenzamide (Orii, Nakamura, Takaki, Sasada & Kakudo, 1963). This kind of twisting may be explained in terms of the steric hindrance between the atoms in the amide or carboxylic group and the atom in the *ortho* position of the ring. In order to examine this hypothesis more quantitatively, the distances between the atoms have been calculated for several

related compounds. Table 10 shows the distances between the atoms in the amide or carboxylic group and the *ortho* position atoms of the ring. Nearly the same value of the interatomic distance is found for a particular pair of these non-bonded atoms. This observation suggests that each atom has the characteristic non-bonded contact radius shown in Table 11, where the aromatic C–H group is treated as a hypothetical atom. These radii are about 0.1 Å less than the ordinary van der Waals radii of the atoms and will be justified by qualitative consideration of the direction-dependence of van der Waals radii (Pauling, 1960).

It may be concluded that the twisting of the amide group around the bond connecting the ring carbon and the amide carbon results mainly from the non-bonded contact between oxygen and the atom in the *o*-position and between nitrogen and the atom in the *o'*-position of the ring.

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References

- ASHIDA, T., HIROKAWA, S. & OKAYA, Y. (1965). *Acta Cryst.* **18**, 122.
 ASHIDA, T., HIROKAWA, S. & OKAYA, Y. (1966). *Acta Cryst.* **21**, 506.
 BAK, B., HANSEN, L. & RASTRUP-ANDERSEN, J. (1954). *J. Chem. Phys.* **22**, 2013.
 CRUICKSHANK, D. W. J. (1956a). *Acta Cryst.* **9**, 754.
 CRUICKSHANK, D. W. J. (1956b). *Acta Cryst.* **9**, 915.
 CRUICKSHANK, D. W. J. (1956c). *Acta Cryst.* **9**, 757.
 CRUICKSHANK, D. W. J. (1957). *Acta Cryst.* **10**, 504.
 HIROKAWA, S. & ASHIDA, T. (1961). *Acta Cryst.* **14**, 774.
 HIRSHFELD, F. L. & RABINOVICH, D. (1965). *Acta Cryst.* **19**, 235.

Table 11. *Intramolecular distances between the atom at the ortho position of the pyridine ring and the amide or carboxyl group (Å)*

Approach	MBAM	SAC	SAM	NAC	BAC	PAM	APAM	BAM	NAM	Average
N–C	2.89	—	2.92	—	—	—	—	2.83	2.91	2.89
O–C	2.87	2.79	—	(2.81 2.80)	(2.79 2.75)	2.82	2.82	2.84	2.77	2.81
N–N	—	—	—	—	—	2.71	2.72	—	—	2.72

Non-bonded contact radii for C, N, O
 Carbon 1.5 Å, Nitrogen 1.4 Å, Oxygen 1.3 Å.

MBAM *m*-methylbenzamide, SAC salicylic acid, SAM salicylamide, NAC nicotinic acid, BAC benzoic acid, PAM picolinamide, APAM α -pyrazinamide, BAM benzamide, NAM nicotinamide.

International Tables for X-ray Crystallography (1962). Vol. III, p.202. Birmingham: Kynoch Press.
 LONGUET-HIGGINS, H. C. & COULSON, C. A. (1947). *Trans. Faraday Soc.* **43**, 87.
 ORII, S., NAKAMURA, T., TAKAKI, Y., SASADA, Y. & KAKUDO, M. (1963). *Bull. Chem. Soc. Japan*, **36**, 788.
 PENFOLD, B. R. & WHITE, J. C. B. (1959). *Acta Cryst.* **12**, 130.
 PAULING, L. (1960). *The Nature of the Chemical Bond*. Ithaca: Cornell Univ. Press.
 ROBERTSON, J. M., SHEARER, H. M. M., SIM, G. A. & WATSON, D. G. (1962). *Acta Cryst.* **15**, 1.

SASADA, Y., TAKANO, T. & KAKUDO, M. (1964). *Bull. Chem. Soc. Japan*, **37**, 940.
 SIM, G. A., ROBERTSON, J. M. & GOODWIN, T. H. (1955). *Acta Cryst.* **8**, 157.
 TAKAKI, Y., SASADA, Y. & WATANABÉ, T. (1960). *Acta Cryst.* **13**, 693.
 TAKAKI, Y. & SASADA, Y. (1966). To be published.
 TAMURA, C., KUWANO, H. & SASADA, Y. (1961). *Acta Cryst.* **14**, 693.
 WILSON, A. J. C. (1942). *Nature, Lond.* **150**, 151.
 WRIGHT, W. B. & KING, G. S. (1954). *Acta Cryst.* **7**, 283.

Acta Cryst. (1966). **21**, 522

The Crystal and Molecular Structure of Lead Hexa-antipyrene Perchlorate

BY M. VIJAYAN AND M. A. VISWAMITRA*

Department of Physics, Indian Institute of Science, Bangalore 12, India

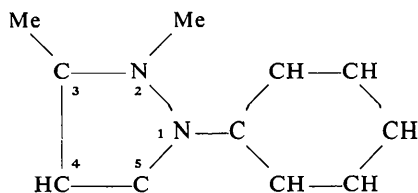
(Received 18 January 1966)

Lead hexa-antipyrene perchlorate is isomorphous with a series of metal hexa-antipyrene perchlorates, $M(C_{11}H_{12}ON_2)(ClO_4)_2$, where $M = Mg^{2+}$, Ca^{2+} or Zn^{2+} , and crystallizes in a hexagonal unit having dimensions $a = 14.33 (\pm 0.03)$, $c = 9.75 (\pm 0.03)$ Å and space group $P\bar{3} (C_{3i}^2)$. The solution of the structure in the c -axis projection was facilitated by the heavy-atom method using ($hki0$) reflexions. A knowledge of the z coordinates obtained previously from a study of the magnesium compound was utilized to work out the complete structure and the refinement was done by the three-dimensional least-squares method to an agreement index of 0.079 for 736 observed reflexions.

In the structure, each Pb^{2+} ion is surrounded by six antipyrene oxygen atoms in a slightly distorted octahedral form with $Pb-O(6) = 2.446 (\pm 0.016)$ Å. The five-membered pyrazolone ring is planar and is inclined at an angle of 68° to the phenyl ring. The tetrahedral ClO_4 ions occupy voids provided by the adjacent antipyrene groups. The two non-equivalent Cl-O bonds, corrected for effects of thermal oscillation, have lengths 1.453(1) and 1.457 Å(3) respectively.

Introduction

1-Phenyl-2,3-dimethyl-5-pyrazolone, $C_{11}H_{12}ON_2$, commonly known as antipyrene, is used as an antipyretic and is of high medicinal interest. Its chemical formula is schematized below:



Its high dipole moment (4.6 to 6.0 D) favours its acting as a coordinating ligand to a large number of metal ions through the oxygen atom in the keto group. Several metal-antipyrene complexes, including those of transition metals and rare-earths, have been synthesized

(Schuyten, 1898, 1900; Kolb, 1913; Dörfurt & Schliephake, 1928, 1929). However, data concerning their crystal structure have not been reported in the literature, except in the case of $Tb(C_{11}H_{12}ON_2)_6I_3$, which crystallizes in the rhombohedral space group $R\bar{3} (C_{3i}^2)$ (Van Uitert & Soden, 1961). Additional structural details of this investigation are not available. Hence it was thought worth while to undertake detailed X-ray studies of these complexes and enquire into the nature of the metal-oxygen bonding in them, besides elucidating the geometry of the antipyrene ring system.

Lead hexa-antipyrene perchlorate is isomorphous with a series of metal hexa-antipyrene perchlorates, $M(C_{11}H_{12}ON_2)_6(ClO_4)_2$, where $M = Mg$, Ca or Zn (all divalent). As part of a programme of X-ray studies on antipyrene complexes, the first structure to be analysed in this laboratory was that of the magnesium compound, $Mg(C_{11}H_{12}ON_2)_6(ClO_4)_2$, which is at present in the final stages of three-dimensional least-squares refinement (Vijayan & Viswamitra, 1965). The isomorphism of the lead compound with the magnesium compound was rather surprising in view of the appreciable

* Present address: Chemical Crystallography Laboratory, South Parks Road, Oxford, England.