The Crystal Structure of Dipicolinic Acid Monohydrate

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The crystal structure of the dipicolinic acid monohydrate has been determined by the method of X-ray diffraction. The crystal is orthorhombic, with a space group of $P2_12_12_1$ and with cell dimensions of $a=12.233$, $b=9.399$, and $c=6.817$ Å. The crystal structure was solved by an inspection of the Patterson map. The final R value was 5.67% for 964 observed reflections. The pyridine ring has the C_{2v} symmetry within the limits of experimental error. The protonation does not occur on the nitrogen atom of the pyridine ring, and two carboxyl groups consist of carbonyl and hydroxyl groups. There is a simple relation between the C–O bond length and the C–C–O bond angle. The molecules are arranged in layers closely parallel to the (0 0 1) plane. Each molecule on the same plane is hydrogen-bonded to form an endless chain along the b axis. These two chains on the planes at $z=1/8$ and 3/8 are linked together by the O–H···N hydrogen bond between the water and pyridine ring to form a double chain along the b axis. In this case, the angle between the N···H(7) vector of the hydrogen bond and the plane of the pyridine ring is 28°. This situation can be explained by the fact that two adjacent and bulky carboxyl groups wrap up the nitrogen atom as an acceptor of the hydrogen bond. The double chains are packed only by the van der Waals forces. The thermal diffuse scattering observed on Weissenberg photographs can be explained by this hydrogen-bond system.

This work is a part of series of X-ray diffraction studies on the O–H···N hydrogen bonding system in pyridine-dicarboxylic acids, which also cover dinicotinic acid,[1] quinolinic acid,[1] and cinchomeronic acid.[1] In connection with this work, the crystal structures of nicotinic acid[2] and benzoic acid[3] have also been established; they all have similar frameworks and isoelectronic structures. However, these two structures were found to be quite different from each other in the way of hydrogen-bond formation. The most remarkable feature is that the hydroxyl group in nicotinic acid is hydrogen-bonded not to the oxygen atom but to the nitrogen atom, although the hydrogen bond is plausible between two carboxyl groups, as in benzoic acid. This was explained by Wright and King[2] on the basis of the packing mode of the moelcules, which does not permit the O–H···O hydrogen bond in this case. Hence, it is of interest to elucidate the effect of the nitrogen atom in the pyridine ring on the hydrogen-bond formation in solids. The crystal structures of calcium dipicolinate trihydrate,[4] strontium dipicolinate tetrahydrate,[5] and some coordination compounds[6–8] containing dipicolinate were also determined by the X-ray method. It is also of interest to compare the molecular dimensions of dipicolinic acid itself with those of its salts and coordination compounds.

Experimental

The crystals were obtained in the form of colorless prisms by recrystallization from an aqueous solution. Weissenberg photographs showed the crystals to be orthorhombic, with the space group of $P2_12_12_1$. The unit cell dimensions were measured from zero-layer Weissenberg photographs taken with Cu$K\alpha$ radiation ($\lambda=1.5418$ Å); these photographs were calibrated with the superimposed Al powder lines ($a=4.0494$ Å). They are given, along other crystal data, in Table 1. There are four molecules in the unit cell, corresponding to the density of 1.56 g/cm³ observed by the flotation method. One crystal was in the shape of a sphere with the average diameter of 0.4 mm. The intensity data were collected for the 0—10 layers around the a axis and the 0—6 layers around the c axis by the use of the multiple-film equi-inclination integrating Weissenberg technique, with Cu$K\alpha$ radiation. The intensities of the diffraction spots

Table 1. Crystal data for dipicolinic acid monohydrate

Molecular formula	$C_7H_5NO_4\cdot H_2O$
Molecular weight	185.14
Crystal size	~0.4×0.4×0.4 mm
Crystal system	Orthorhombic
Space group	$P2_12_12_1$
Cell dimensions;	
a	12.233±0.003 Å
b	9.399±0.001
c	6.817±0.006
V	783.8±0.8 Å³
Z	4
Density (calculated)	1.569 g/cm³
Density (observed)	1.56
Radiation	Cu$K\alpha$ ($\lambda=1.5418$ Å)
Linear absorption coefficient	13.54 cm^{-1}
Number of independent reflections	1026
The atom numbering	

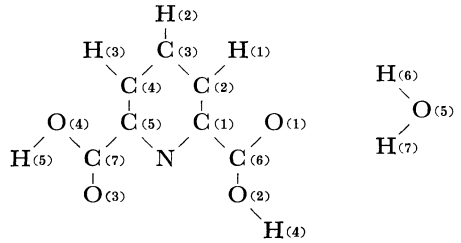

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Table 2. THE OBSERVED AND CALCULATED STRUCTURE FACTORS.

F_O, F_C and DF have been multiplied by 10. The unobserved reflections are indicated by an asterisk. The reflections, for which the $|F_O-F_C|/|F_O|$ is larger than 0.3, are indicated by a plus sign.

H	FO	FC	DF	H	FO	FC	DF	H	FO	FC	DF	H	FO	FC	DF	H	FO	FC	DF	H	FO	FC	DF	H	FO	FC	DF
K,L= 0	0			11*	0	4	-4	6	100	99	1	K,L= 9	1			1	73	72	0	2	54	48	6	8	19	19	0
2	750	779	-29	12*	0	4	-4	7	89	94	-4	0	121	111	10	2	345	346	0	3+	35	23	11	9	27	30	-2
4	429	443	-14	13	36	34	1	8	45	43	1	1	49	42	7	3	204	191	13	4	95	95	0	10	50	53	-3
6	401	407	-5	K,L= 7	0			9	46	48	-1	2	68	69	-1	4	241	229	11	5	110	108	2	11	17	19	-2
8	210	198	12	1	94	84	10	10+	17	8	8	3	55	55	0	5	132	134	-2	6	22	22	0	12	11	13	-2
10	175	179	-4	2	157	161	-4	11*	0	13	-13	4	55	51	3	6	56	54	1	7+	12	7	4	K,L= 7		3	
12	103	99	3	3	42	41	1	12	40	40	0	5	45	41	3	7	56	54	2	8	53	49	3	0	42	44	-1
14	76	60	16	4*	0	0	0	13	40	40	0	6	29	30	-1	8	192	198	-5	9	30	32	-2	1	30	33	-2
K,L= 1	0			5	63	64	0	14	19	18	0	7	48	49	-1	9	82	81	0	10*	0	8	-8	2	64	66	-2
1	59	62	-2	6	104	111	-6	15	20	14	5	8	35	28	6	10	108	106	2	11	44	44	0	3	61	65	-3
2	319	327	-8	7	25	31	-5	K,L= 3		1		9	38	36	1	11	15	14	0	12	18	18	0	4	39	40	-1
3	176	187	-10	8	49	56	-7	0	21	24	-2	10	38	36	1	12	35	34	0	13	16	18	-2	5	62	66	-4
4	215	209	6	9	88	88	0	1	218	222	-4	K,L= 10		1		13	36	39	-3	14	9	10	-1	6	27	27	0
5	213	209	4	10+	11	7	3	2	266	267	0	0	83	74	9	14	11	11	0	K,L= 1		3		7	16	15	0
6	102	98	4	11	45	42	2	3	259	260	0	1	56	50	6	K,L= 5		2		0	115	110	5	8	26	29	-2
7	81	75	5	12	45	40	5	4	239	239	0	2	31	28	3	0	14	14	0	1	141	123	18	9+	11	5	6
8	96	86	9	K,L= 8	0			5	124	126	-1	3	47	44	2	1	82	82	0	2	161	146	15	10	12	10	2
9	66	52	14	0	37	34	3	6	61	60	0	4	43	43	0	2	55	51	3	3	99	82	17	11+	11	18	-6
10	20	18	1	1	47	47	0	7	136	141	-5	5	77	71	6	3	174	171	3	4	90	88	1	K,L= 8		3	
11	83	85	-1	2	82	84	-2	8	189	201	-12	6	46	41	5	4	73	74	0	5	122	106	15	0	163	160	2
12	53	48	5	3	19	21	-1	9	179	176	3	7	23	23	0	5	52	51	0	6	155	148	7	1	294	287	7
13	71	70	0	4	15	15	0	10	191	181	9	8	15	16	0	6	34	32	2	7	154	150	3	2	119	125	-6
14	19	21	-2	5	31	32	0	11	112	106	6	K,L= 11		1		7	172	174	-2	8	49	53	-3	3	114	116	-2
15	27	21	5	6	22	22	0	12	63	58	4	0	37	34	3	8	195	209	-13	9	22	23	0	4	24	27	-3
K,L= 2	0			7	29	29	0	13+	18	11	6	1	42	39	2	9	75	71	4	10	48	49	-1	5	82	93	-10
0	234	261	-27	8	84	81	2	14	22	15	6	2	35	30	4	10	41	40	1	11	92	93	-1	6	43	46	-3
1	229	235	-6	9	26	26	0	15	36	31	4	3	82	79	3	11	87	92	-4	12	62	67	-5	7	64	68	-4
2	410	402	8	10*	0	0	0	K,L= 4		1		4	75	72	3	12	15	12	3	13+	14	19	-4	8	51	51	0
3	218	230	-11	11	15	12	2	0	100	97	2	5	37	30	6	13	19	18	0	14	13	16	-2	9	32	31	1
4	593	588	4	K,L= 9	0			1	448	449	0	6+	17	11	5	K,L= 6		2		K,L= 2		3		10	34	36	-1
5	141	143	-1	1	29	26	2	2	397	388	8	K,L= 12		1		0	24	23	1	0+	11	4	7	K,L= 9		3	
6	135	133	1	2*	0	9	-9	3	231	233	-2	0	75	64	11	1	127	129	-1	1	82	77	4	0	84	81	2
7	129	144	-14	3	14	14	0	4	122	111	11	K,L= 0		2		2	115	114	0	2	243	230	13	1	49	50	-1
8	12	9	3	4	75	78	-2	5	116	106	10	0	461	478	-16	3	130	128	2	3	71	72	-1	2	37	39	-1
9+	28	19	8	5	71	74	-2	6	52	59	-6	1	657	1678	-21	4	43	41	2	4	128	115	12	3	42	45	-2
10	24	19	4	6	44	49	-5	7	118	120	-2	2	243	250	-6	5	62	62	0	5	120	115	4	4	24	23	0
11	65	61	4	7	14	12	2	8	189	186	3	3	192	181	11	6	19	19	0	6	44	42	1	5	32	31	0
12	39	33	5	8	37	37	0	9	190	193	-3	4	124	117	6	7	64	64	0	7	95	96	0	6	22	23	0
13*	0	1	-1	9	69	57	11	10	49	46	3	5	328	302	26	8	27	28	-1	8+	13	7	5	7	22	27	-4
14	25	20	5	10	75	65	9	11	44	38	6	6	67	60	7	9	11	13	-1	9	29	29	0	8	22	24	-2
15+	20	13	7	K,L= 10	0			12	25	23	1	7	327	315	11	10	26	27	0	10	27	30	-2	K,L= 10		3	
K,L= 3	0			0	18	19	0	13	31	27	3	8	41	39	1	11	11	12	-1	11*	0	6	-6	0	27	28	-1
1	181	189	-7	1	25	24	0	14	22	18	4	9	82	85	-3	12	10	13	-2	12	22	24	-2	1	43	42	0
2	178	182	-4	2	12	10	2	K,L= 5		1		10	28	23	5	13	15	16	-1	13	21	25	-4	2	15	19	-3
3	314	326	-11	3	15	11	3	0	100	104	-3	11	86	83	2	K,L= 7		2		14*	0	5	-5	3	25	25	0
4	49	43	6	4	86	87	0	1	59	54	4	12	25	20	4	0	87	92	-4	K,L= 3		3		4	27	28	0
5	108	115	-6	5	81	77	4	2	167	172	-4	13	87	94	-7	1	42	40	2	0	33	33	0	5	29	29	0
6*	0	8	-8	6	56	49	6	3	131	126	5	14	17	18	-1	2	50	51	0	1	20	22	-1	6	34	37	-3
7*	0	14	-14	7+	14	9	5	4	19	21	-2	15	8	6	1	3	120	122	-1	2	187	164	23	K,L= 11		3	
8	22	23	0	8	15	16	0	5	109	105	3	K,L= 1		2		4	53	56	-3	3	188	180	8	0	32	37	-5
9	189	193	-3	K,L= 11	0			6	80	81	0	0	184	187	-2	5	27	29	-1	4	85	85	0	1+	7	4	3
10	82	82	0	1	110	97	13	7	88	92	-4	1	538	561	-22	6	18	16	1	5	69	73	-4	2	28	30	-2
11	70	58	12	2	22	17	5	8	126	128	0	2	87	89	-2	7	106	122	-16	6	31	38	-6	3	38	42	-4
12*	0	14	-14	3	54	47	6	9	158	160	-1	3	214	212	2	8	50	56	-5	7	77	79	-2	K,L= 0		4	
13	82	76	6	4	63	54	8	10	89	87	1	4	27	24	2	9	19	17	1	8	157	149	8	1	299	284	15
14	44	43	0	5+	33	22	11	11	41	34	6	5	34	32	2	10	28	29	0	9	141	136	4	2	153	171	-17
15	23	19	4	6	20	18	1	12	29	29	0	6	155	157	-1	11	12	14	-1	10	84	81	2	3	141	140	1
K,L= 4	0			K,L= 12	0			13	14	15	0	7	41	44	-2	12	73	72	0	11	83	95	-12	4	139	122	17
0	374	392	-17	0	145	132	12	14	52	48	4	8	43	42	1	K,L= 8		2		12	34	36	-1	5	78	77	1
1	302	306	-4	1	66	51	15	K,L= 6		1		9	76	71	5	0	18	17	1	13	15	18	-2	6	150	141	8
2	335	333	1	K,L= 0		1		0	19	23	-3	10	13	14	0	1	31	29	2	14	11	10	0	7	48	50	-2
3	425	455	-29	1	238	220	17	1	50	53	-3	11	14	15	-1	2	33	36	-2	K,L= 4		3		8	68	67	0
4	142	136	6	2	24	20	3	2	144	155	-11	12	64	68	-3	3+	14	9	4	0+	18	10	8	9+	10	3	6
5	146	150	-3	3	45	42	3	3	215	222	-6	13	25	26	-1	4	28	29	-1	1	189	177	12	10	76	76	0
6	129	120	9	4	150	148	2	4	103	94	9	14	27	31	-4	5	23	25	-2	2	270	261	9	11	32	30	1
7	134	137	-3	5	136	121	14	5	58	57	0	15	15	10	4	6	25	29	-4	3	84	85	-1	12	40	42	-1
8	35	40	-4	6	49	44	5	6	20	21	0	K,L= 2		2		7	53	50	2	4	127	122	5	13+	15	21	-6
9	232	251	-19	7	97	91	6	7	61	61	0	0	59	55	3	8	37	40	-2	5	25	23	2	14+	15	23	-7
10	84	85	-1	8	69	71	-2	8	22	24	-2	1	324	314	10	9	11	10	1	6	44	43	0	K,L= 1		4	
11*	0	1	-1	9	100	93	6	9	47	51	-4	2	204	199	4	10	12	11	0	7	82	84	-2	0	40	42	-1
12*	0	2	-2	10	23	26	-2	10	72	71	0	3	236	224	12	11	30	30	0	8	172	172	0	1	84	84	0
13	25	18	7	11	32	36	-3	11	54	48	5	4	113	110	2	K,L= 9		2		9	78	78	0	2	120	109	10
14	47	40	7	12	21	18	2	12+	25	14	10	5	121	121	0	0	27	26	0	10	59	64	-5	3	60	57	2
K,L= 5	0			13	58	52	5	K,L= 7		1		6	110	110	0	1	23	25	-1	11	18	22	-3	4	62	53	9
1	17	19	-1	14	16	13	2	0	55	58	-2	7	59	54	4	2	25	25	0	12	22	28	-6	5	48	48	0
2	104	104	0	15+	13	8	5	1	50	49	1	8	44	40	3	3	12	14	-2	13	14	14	0	6	27	26	0
3+	26	16	9	K,L= 1		1		2	77	81	-3	9	19	17	1	4	27	29	-1	K,L= 5		3		7	24	29	-4
4	120	116	4	0	190	193	-2	3	70	71	0	10	26	26	0	5	79	85	-6	0	50	52	-2	8	46	49	-3
5	158	140	17	1	276	270	5	4	124	127	-3	11	55	60	-4	6	62	64	-1	1+	13	5	8	9	19	23	-3
6	197	200	-3	2	144	147	-3	5	68	71	-2	12	37	36	1	7	11	9	1	2	140	140	0	10*	0	0	0
7	160	176	-16	3	198	193	4	6	56	55	1	13	34	35	-1	8	33	32	1	3	63	56	6	11	25	25	0
8	116	110	5	4	203	193	10	7	18	17	0	14	18	17	0	9	13	13	0	4	35	30	5	12	22	29	-6
9	169	176	-7	5	162	159	2	8	28	28	0	K,L= 3		2		K,L= 10		2		5	25	28	-3	13+	16	22	-5
10	132	134	-2	6	276	306	-29	9+	13	3	9	0	74	68	5	0*	0	2	-2	6	83	83	0	K,L= 2		4	
11*	0	9	-9	7	206	199	7	10	25	25	0	1	120	121	0	1	17	20	-2	7	68	73	-4	0	54	52	1
12	46	37	8	8	158	147	11	11	13	10	3	2	198	195	2	2	35	34	0	8	82	85	-3	1	78	69	8
13	24	17	6	9+	46	22	24	12	22	16	6	3	262	252	10	3	66	69	-3	9	85	87	-1	2	102	100	1
14	49	37	11	10	106	104	1	K,L= 8		1		4	202	185	16	4	36	38	-1	10	83	86	-2	3	63	55	8
K,L= 6	0			11	116	112	4	0	380	416	-35	5	131	133	-2	5	23	18	4	11+	14	20	-6	4	175	163	12
0	136	148	-12	12	98	93	4	1	315	330	-14	6	13	13	0	6	25	23	2	12+	13	18	-4	5	33	32	0
1	116	117	-1	13	31	26	5	2	264	260	4	7	87	92	-5	7	9	10	0	13	15	13	2	6	56	57	0
2	62	60	1	14	16	12	4	3	99	101	-1	8	71	68	3	K,L= 11		2		K,L= 6		3		7	32	32	0
3	69	68	1	15	19	17	1	4	112	113	-1	9	44	45	-1	0	70	64	6	0	13	12	1	8*	0	9	-9
4	181	179	2	K,L= 2		1		5	76	84	-7	10	139	144	-4	1	37	36	0	1	32	29	2	9+	10	5	5
5	63	66	-2	0	15	17	-2	6	102	109	-6	11	49	46	2	2	74	73	1	2	117	119	-2	10*	0	7	-7
6	190	197	-7	1	167	165	1	7	66	69	-3	12	43	44	0	3	23	22	0	3	79	81	-2	11	22	26	-3
7	24	20	4	2	343	345	-2	8	61	68	-7	13+	11	6	4	4+	10	7	3	4	40	40	0	12*	0	4	-4
8	13	11	1	3	237	238	0	9	73	70	2	14	20	23	-3	5	37	38	-1	5	43	48	-5	13*	0	1	-1
9	47	46	0	4	206	205	1	10	61	57	3	K,L= 4		2		K,L= 0		3		6	16	19	-2	K,L= 3		4	
10	31	31	0	5	325	331	-5	11	50	44	5	0	56	46	9	1	21	27	-5	7	25	29	-3	0	47	39	7

TABLE 2. Continued.

H	FO	FC	DF	H	FO	FC	DF	H	FO	FC	DF	H	FO	FC	DF	H	FO	FC	DF	H	FO	FC	DF	H	FO	FC	DF
1	15	14	0	5	12	10	1	K=L=	2	5		5	24	26	0	11	7	5	1	0	46	43	3	2	38	39	0
2	100	103	-2	6	39	39	0	0	18	17	1	6	9	8	1	K=L=	2	6		1	33	31	2	3*	0	5	-5
3	96	98	-2	7	25	24	1	1	38	33	5	7	14	12	1	0	14	12	2	2	30	31	-1	4	28	30	-2
4	39	38	0	8	20	21	-1	2	43	40	3	6+	3	3	4	1	32	34	-1	3	32	33	0	5	8	7	1
5	51	48	2	9	29	32	-3	3	60	61	0	9	12	13	-1	2	22	23	-1	4	11	10	0	6	23	24	-1
6	25	25	0	10	9	7	1	4	33	32	1	10	15	19	-3	3	16	15	0	5	11	11	0	7+	10	26	-16
7	24	28	-4	K=L=	8	4		5	64	62	2	K=L=	7	5		4	15	19	-3	6	13	10	3	K=L=	5	7	
8	45	45	0	0+	12	2	9	6	30	30	0	0+	9	4	5	5	12	11	1	7	20	23	-2	0	14	13	0
9	63	69	-5	1	15	18	-3	7	44	40	4	1	29	28	1	6	10	7	2	K=L=	8	6		1	15	13	1
10	52	57	-4	2	33	33	0	8*	0	9	-9	2	25	26	0	7	11	8	2	0	10	8	1	2	14	15	-1
11	26	32	-5	3	18	18	0	9	20	22	-2	3	14	12	2	8	3	2	0	1	15	15	0	3	23	24	-1
12*	0	8	-8	4	22	23	0	10	22	20	1	4	39	39	0	9*	0	3	-3	2	8	6	2	4*	0	3	-3
13+	26	34	-8	5	30	32	-1	11	9	10	-1	5	9	8	0	10*	0	5	-5	3	9	11	-1	5	9	9	0
K=L=	4	4		6	14	14	0	12	9	9	0	6	21	21	0	11	9	8	0	4	11	13	-2	6	15	16	0
0	132	124	8	7	22	26	-3	K=L=	3	5		7	10	10	0	K=L=	3	6		5*	0	9	-9	7	23	21	1
1	108	103	5	8	22	25	-2	0	34	27	6	8	6	5	1	0	27	25	2	K=L=	0	7		K=L=	6	7	
2	109	105	3	9	11	13	-1	1	34	33	0	9	8	9	0	1	17	14	2	1+	19	11	8	0*	0	1	-1
3	162	155	6	K=L=	9	4		2	33	35	-1	K=L=	8	5		2	13	14	-1	2*	0	2	-2	1	14	12	2
4	64	60	4	0+	13	18	-5	3	20	21	0	0	178	172	5	3	64	62	1	3+	12	7	4	2	10	10	0
5	48	51	-2	1	26	28	-1	4	70	69	1	1	60	66	-6	4	35	35	0	4	23	24	-1	3	9	9	0
6	66	71	-5	2	14	18	-3	5	12	13	-1	2	106	107	-1	5	13	11	1	5	12	13	-1	4*	0	2	-2
7	52	53	-1	3	12	11	0	6	16	15	0	3	10	12	-2	6	21	19	2	6	23	16	6	K=L=	7	7	
8	49	50	-1	4	29	32	-3	7	55	55	0	4	60	60	0	7	29	28	1	7+	6	1	4	0*	0	0	0
9	105	117	-12	5	35	39	-3	8	70	65	4	5	10	10	0	8	19	17	2	8+	12	8	3	1	8	10	-2
10	50	54	-4	6+	11	17	-6	9	50	48	2	6	44	50	-5	9	27	26	0	9	7	7	0	K=L=	0	8	
11	11	10	0	7+	12	15	-3	10	71	71	0	7	11	11	0	10	27	30	-3	K=L=	1	7		0	89	73	16
12*	0	8	-8	K=L=	10	4		11	19	23	-3	K=L=	9	5		K=L=	4	6		0	58	50	8	1	63	58	5
K=L=	5	4		0	6	6	0	12	22	26	-4	0	48	50	-1	0	29	25	4	1*	0	8	-8	2	17	18	0
0	13	14	0	1	11	12	-1	K=L=	4	5		1	24	26	-1	1	24	23	1	2	41	43	-1	3	35	37	-1
1	27	31	-4	2	9	8	0	0	15	13	2	2	15	16	0	2	60	60	0	3	19	19	0	4	10	9	1
2	16	14	1	3	12	16	-3	1	107	105	1	3+	8	11	-3	3	38	37	1	4*	0	9	-9	5	21	24	-2
3	46	48	-1	4+	20	27	-6	2	44	47	-3	4	18	21	-2	4	41	42	-1	5	9	8	1	6	13	15	-2
4	31	27	4	5	18	20	-2	3	70	68	1	5	11	12	0	5	35	39	-3	6	36	33	3	K=L=	1	8	
5	39	42	-2	K=L=	0	5		4*	0	7	-7	K=L=	10	5		6+	14	8	5	7+	23	13	9	0*	0	2	-2
6	74	75	-1	1	50	48	1	5	54	59	-5	0*	0	19	-19	7	39	37	1	8+	8	3	5	1	20	20	0
7	83	90	-6	2	35	28	6	6	32	31	1	K=L=	0	6		8	45	47	-2	9	11	9	2	2	14	15	0
8	51	52	-1	3*	0	4	-4	7	68	63	4	0	161	157	4	9	33	40	-6	K=L=	2	7		3*	0	2	-2
9	70	73	-2	4	34	34	0	8	52	54	-2	1	181	185	-4	10	25	30	-5	0	12	8	3	4*	0	3	-3
10	58	61	-3	5	68	68	0	9	88	87	0	2	96	100	-4	K=L=	5	6		1*	0	7	-7	5*	0	2	-2
11	24	29	-4	6	14	14	0	10	10	8	1	3	16	14	2	0	17	17	0	2	22	25	-3	6*	0	0	0
12	16	20	-3	7*	0	1	-1	11	15	18	-2	4	66	64	2	1	21	21	0	3*	0	0	0	K=L=	2	8	
K=L=	6	4		8	15	14	0	K=L=	5	5		5	48	49	0	2	25	27	-1	4*	0	4	-4	0*	0	7	-7
0	54	52	1	9	29	26	3	0	35	37	-2	6	36	35	1	3	14	15	-1	5+	9	5	4	1*	0	7	-7
1	51	53	-1	10	35	30	5	1	17	15	1	7	53	52	1	4	17	17	0	6	12	9	2	2	12	12	0
2	25	28	-2	11	17	21	-4	2	44	40	4	8	17	18	-1	5	9	8	1	7	14	14	0	3*	0	4	-4
3	27	28	-1	12	8	7	0	3	47	47	0	9	22	21	0	6	20	22	-2	8	10	8	2	4	10	8	1
4	51	56	-5	K=L=	1	5		4	26	24	2	10	21	19	2	7	35	35	0	9	13	14	-1	5*	0	1	-1
5	21	20	0	0	44	43	1	5	31	32	-1	11	18	18	0	8	44	51	-6	K=L=	3	7		K=L=	3	8	
6	78	74	3	1	109	103	5	6	19	14	5	K=L=	1	6		9	16	19	-3	0+	12	8	4	0*	0	1	-1
7	25	25	0	2	29	26	2	7	30	24	5	0	71	65	5	K=L=	6	6		1*	0	9	-9	1	11	10	0
8	23	24	-1	3+	18	12	5	8	54	59	-4	1	71	70	1	0	18	15	2	2*	0	8	-8	2	15	16	0
9	27	29	-1	4	36	27	8	9	55	57	-1	2	12	9	3	1	15	16	0	3	22	23	-1	3	10	12	-1
10	7	6	1	5	53	51	2	10	19	20	0	3	13	11	1	2	25	24	0	4	10	9	1	4	9	11	-2
11*	0	3	-3	6	59	60	-1	11	9	11	-2	4	12	10	1	3	20	19	1	5	13	15	-2	5*	0	11	-11
K=L=	7	4		7	32	29	3	K=L=	6	5		5*	0	4	-4	4	9	9	0	6	16	13	2	K=L=	4	8	
0	26	27	-1	8	24	29	-5	0	22	19	2	6	16	18	-2	5	17	14	2	7+	11	19	-8	0+	10	5	5
1	72	72	0	9	9	7	2	1	12	12	0	7*	0	3	-3	6	12	9	3	8	28	32	-3	1	15	14	0
2	75	77	-2	10	48	44	4	2	22	24	-1	8+	7	5	2	7+	9	4	4	K=L=	4	7		2	13	17	-3
3	22	25	-2	11	33	35	-1	3	46	47	0	9	23	21	2	8	7	6	0	0+	10	6	4	3+	15	20	-5
4*	0	5	-5	12	30	36	-5	4	15	16	0	10*	0	0	0	K=L=	7	6		1*	0	11	-11				

were estimated visually by comparison with an intensity standard. Of the 1071 possible reflections within the Cu$K\alpha$ sphere, 1026 independent reflections were measured; 62 were too weak to be observed. No absorption correction was applied. The appreciable thermal diffuse scattering along the a^* and c^* axes was observed on Weissenberg photographs.

Structure Determination and Refinement

At first, the crystal structure determination was attempted by the symbolic addition method. However, the statistical average for normalized structure factors showed an abnormal distribution as if this crystal had a centro-symmetric structure. Therefore, the phase refinement by the use of the tangent formula did not lead to the determination of the crystal structure. An effort was then made to solve the structure by the Patterson method. The sharpened Patterson map was resolved sufficiently to give the orientation and location of the molecule in the unit cell. The first postulated structure gave an R value of 52%, which decreased to 31% in three cycles of least-squares refinement with individual isotropic thermal factors. A difference Fourier map which was calculated by the use of these parameters clearly showed the position of the water oxygen atom. Since the 0 0 4 reflection seemed to have a strong extinction effect, this reflection was removed from the later refinements.

The coordinates and anisotropic thermal factors were refined in a block-diagonal least-squares procedure, minimizing the function $\sum w(F_o-F_c)^2$, where:

$$w = 0.5 \text{ for } |F_o| \leqq 0.5,$$
$$w = 1.0 \text{ for } 0.5 < |F_o| < 7.0 \text{ and}$$
$$w = 7.0/|F_o| \text{ for } 7.0 \leqq |F_o|.$$

The atomic scattering factors used were those listed in the International Table for X-ray Crystallography for C, N, and O atoms, and the spherical scattering factors proposed by Stewart, Davidson, and Simpson[9] for the H atom. At the stage of $R=7.9\%$, a difference Fourier map was computed, from which the positions of the seven hydrogen atoms were found (Fig. 1). With anisotropic thermal parameters for non-hydrogen atoms and isotropic thermal parameters for hydrogen atoms, the final R value was 5.67%, excluding unobserved reflections. The observed and calculated structure factors are listed in Table 2. The fractional coordinates and thermal parameters are listed in Table 3.

9) R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, **42**, 3175 (1965).

TABLE 3. THE FINAL PARAMETERS AND THEIR ESTIMATED STANDARD DEVIATIONS (IN PARENTHESES)
The coordinates of the non-hydrogen atoms have been multiplied by 10^4; those of the hydrogen atoms, by 10^3. The anisotropic thermal parameters of non-hydrogen atoms are of the form $\exp[-(B_{11}h^2+B_{22}k^2+B_{33}l^2+B_{12}hk+B_{13}hl+B_{23}kl)]$, and have been multiplied by 10^5. For the hydrogen atoms, the values listed are isotropic thermal parameters B(Å^2).

Atom	x	y	z	B(Å^2)	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
N	2166 (2)	2793 (3)	1491 (5)	—	523 (19)	569 (26)	2419 (76)	−64 (38)	256 (80)	−174 (98)
C (1)	2651 (3)	4067 (3)	1396 (7)	—	645 (25)	691 (33)	2188 (88)	−219 (51)	200 (98)	−76 (119)
C (2)	3783 (3)	4246 (4)	1256 (7)	—	662 (27)	811 (38)	2950 (111)	−414 (55)	86 (111)	52 (144)
C (3)	4440 (3)	3066 (4)	1234 (8)	—	485 (24)	1303 (53)	3645 (133)	−389 (59)	110 (117)	−33 (182)
C (4)	3950 (3)	1745 (4)	1312 (8)	—	594 (25)	847 (39)	3472 (124)	230 (55)	22 (118)	−29 (155)
C (5)	2820 (3)	1655 (3)	1443 (7)	—	575 (23)	689 (33)	2369 (91)	−47 (49)	130 (96)	58 (123)
C (6)	1940 (3)	5376 (3)	1388 (7)	—	723 (27)	671 (35)	2509 (96)	−146 (54)	214 (105)	−22 (127)
C (7)	2243 (3)	233 (3)	1496 (7)	—	622 (25)	605 (34)	2802 (104)	105 (49)	197 (105)	43 (129)
O (1)	2367 (2)	6544 (3)	1464 (7)	—	901 (24)	554 (25)	5309 (127)	−338 (44)	681 (116)	−203 (130)
O (2)	900 (2)	5163 (2)	1330 (6)	—	648 (18)	601 (24)	3800 (88)	94 (37)	303 (84)	−205 (103)
O (3)	1285 (2)	81 (3)	1484 (7)	—	602 (18)	605 (26)	5778 (127)	−180 (37)	518 (102)	177 (127)
O (4)	2953 (2)	−816 (3)	1538 (8)	—	695 (21)	530 (25)	6869 (156)	167 (39)	−105 (120)	15 (136)
O (5)	−102 (2)	7556 (3)	1321 (5)	—	569 (18)	729 (26)	3994 (90)	155 (38)	359 (87)	−150 (113)
H (1)	401 (3)	528 (5)	119 (7)	4.9 (0.9)						
H (2)	516 (3)	318 (5)	107 (7)	5.3 (1.0)						
H (3)	434 (3)	100 (4)	126 (7)	4.7 (0.9)						
H (4)	64 (3)	603 (4)	147 (7)	4.1 (0.8)						
H (5)	267 (3)	−153 (5)	151 (7)	6.2 (1.1)						
H (6)	13 (3)	822 (4)	144 (6)	4.6 (0.9)						
H (7)	−65 (5)	744 (7)	190 (9)	9.7 (1.6)						

TABLE 4. INTRAMOLECULAR BOND LENGTHS AND BOND ANGLES

Bond	Length(Å)	e.s.d.(Å)	Bond	Angle(°)	e.s.d.(°)
N −C (1)	1.338	0.005	C (1)−N −C (5)	116.8	0.4
C (1)−C (2)	1.399	0.006	N −C (1)−C (2)	123.4	0.4
C (2)−C (3)	1.372	0.007	N −C (1)−C (6)	118.4	0.4
C (3)−C (4)	1.378	0.007	C (2)−C (1)−C (6)	118.2	0.4
C (4)−C (5)	1.388	0.006	C (1)−C (2)−C (3)	118.9	0.5
C (5)−N	1.336	0.005	C (2)−C (3)−C (4)	118.2	0.5
C (1)−C (6)	1.507	0.006	C (3)−C (4)−C (5)	119.4	0.5
C (5)−C (7)	1.511	0.006	C (4)−C (5)−N	123.3	0.4
C (6)−O (1)	1.217	0.006	C (4)−C (5)−C (7)	121.4	0.4
C (6)−O (2)	1.280	0.005	N −C (5)−C (7)	115.3	0.4
C (7)−O (3)	1.181	0.006	C (1)−C (6)−O (1)	119.2	0.4
C (7)−O (4)	1.315	0.006	C (1)−C (6)−O (2)	116.3	0.4
C (2)−H (1)	1.02	0.05	O (1)−C (6)−O (2)	124.4	0.5
C (3)−H (2)	0.89	0.05	C (5)−C (7)−O (3)	124.8	0.5
C (4)−H (3)	0.85	0.05	C (5)−C (7)−O (4)	110.8	0.4
O (2)−H (4)	0.88	0.05	O (3)−C (7)−O (4)	124.4	0.5
O (4)−H (5)	0.76	0.05	C (1)−C (2)−H (1)	113	3
O (5)−H (6)	0.69	0.04	C (3)−C (2)−H (1)	128	3
O (5)−H (7)	0.79	0.06	C (2)−C (3)−H (2)	119	3
			C (4)−C (3)−H (2)	123	3
			C (3)−C (4)−H (3)	119	3
			C (5)−C (4)−H (3)	121	3
			C (6)−O (2)−H (4)	102	3
			C (7)−O (4)−H (5)	111	4
			H (6)−O (5 (−H (7)	115	5

Results and Discussion

Molecular Structure. The bond lengths and bond angles are listed, along their estimated standard deviations, in Table 4 and are shown in Fig. 2. Figure 1 shows a difference Fourier map along the c axis. There are three peaks around the water oxygen atom. Two of them correspond to the hydrogen atoms of the water molecule, while one may be a ghost peak or a peak due to disordered hydrogen atoms. There is no other

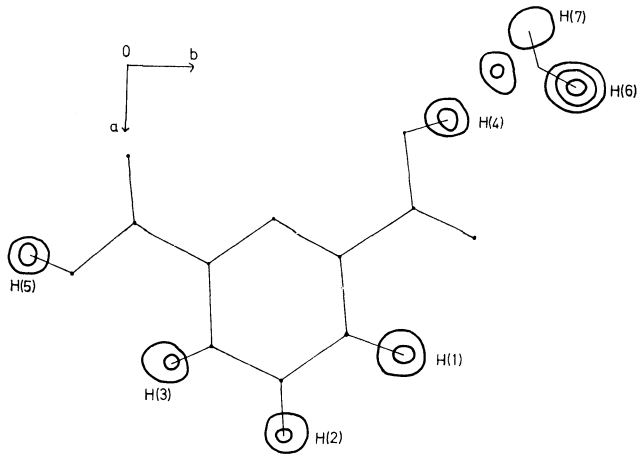


Fig. 1. A composite drawing of the electron density associated with the hydrogen atoms. The contours are at intervals of 0.1 e Å^{-3}, beginning with the 0.3 e Å^{-3} contour.

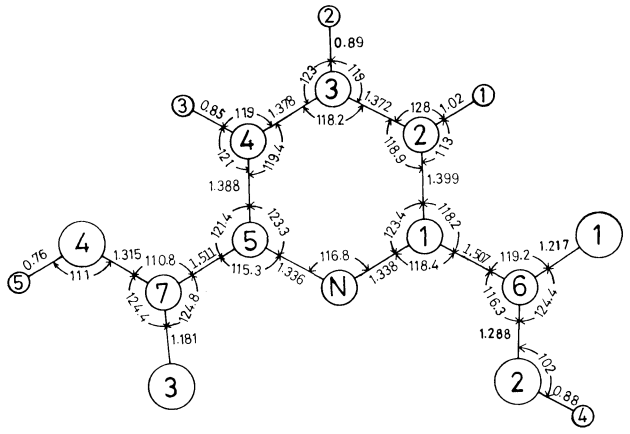


Fig. 2. Dimensions of the dipicolinic acid molecule.

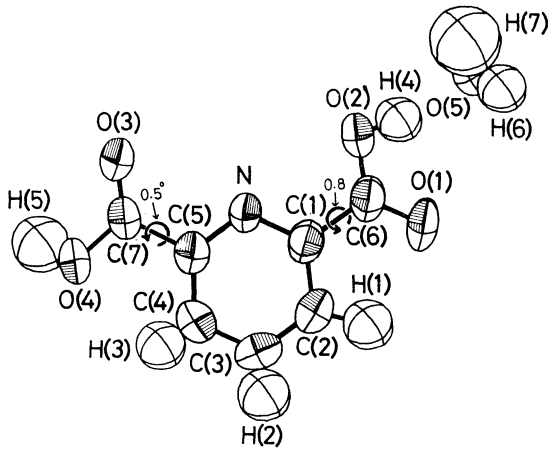


Fig. 3. The anisotropic thermal ellipsoids of non-hydrogen atoms and the isotropic thermal ellipsoids of hydrogen atoms. Ellipsoids are scaled to include 74% probability.

unexplainable peak in this difference Fourier map. Figure 3 shows the anisotropic thermal ellipsoids of non-hydrogen atoms and the isotropic thermal ellipsoids of hydrogen atoms. Ellipsoids are scaled to include 74% probability.

The pyridine ring is planar, and the maximum deviation of a ring atom from the least-squares plane is 0.007 Å. The equation of the least-squares plane through the six non-hydrogen atoms of the pyridine ring is;

$$0.0622X + 0.0208Y + 0.9979Z = 1.2303$$

where X, Y, and Z are coordinates in Å referred to an orthogonal set of axes and parallel to the a, b, and c axes. The displacements of all the atoms from the plane are listed in Table 5.

Table 5. The distances from the least-squares plane defined by the six non-hydrogen atoms of pyridine ring

Atom	Deviation (Å)	Atom	Deviation (Å)
N	−0.004	O (3)	0.121
C (1)	0.000	O (4)	0.025
C (2)	0.005	O (5)	0.192
C (3)	−0.007	H (1)	0.01
C (4)	0.003	H (2)	0.05
C (5)	0.002	H (3)	0.02
C (6)	0.034	H (4)	0.06
C (7)	0.038	H (5)	0.03
O (1)	−0.073	H (6)	0.08
O (2)	0.156	H (7)	−0.16

The comparisons between the corresponding bond lengths and bond angles of dipicolinic acid and calcium dipicolinate,[4] strontium dipicolinate[5] and pyridine[10] are given in Table 6. The pyridine ring has the C_{2v} symmetry within the limits of experimental error. The dimensions of the pyridine ring are in good agreement with those of pyridine itself, except for the C(2)–C(3) and C(3)–C(4) bond lengths. The net charges and π-bond orders calculated by the "complete neglect of the differential overlap (CNDO)" method[11] are shown in Fig. 4. The bond orders of the C(2)–C(3), C(3)–C(4), C(1)–C(2), and C(4)–C(5) bonds are 0.674, 0.659, 0.637, and 0.651 respectively. The first two bond orders are larger than the two others. These are in good correlation with the bond lengths obtained experimentally. The pyridine ring of dipicolinic acid

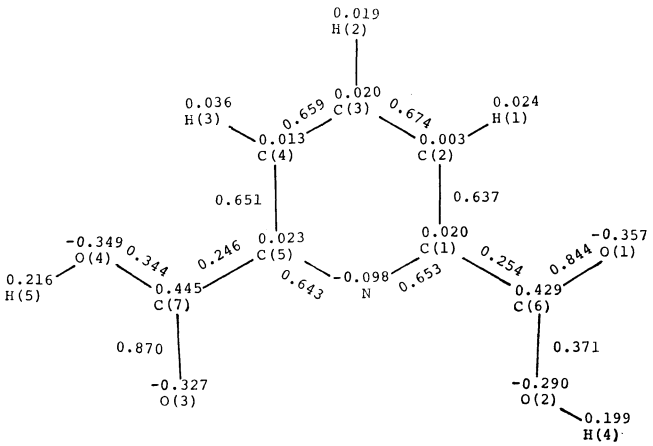


Fig. 4. The net charges and π-bond orders calculated by the CNDO method.

10) B. Bak, L. H. Nygaard, and J. R. Andersen, *J. Mol. Spectrosc.*, **2**, 361 (1958).

11) J. A. Pople and D. L. Beveridge, "Approximate Molecular Orbital Theory," McGraw-Hill Book Co., New York (1970).

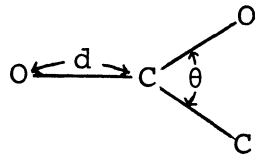
Table 6. The comparisons between the corresponding bond lengths and angles of dipicolinic acid and calcium dipicolinate, strontium dipicolinate and pyridine

Bond length	(a)	(b)	(c)	(d)
N –C (1)	1.338 Å	1.339 Å	1.335 Å	1.340 Å
C (1)–C (2)	1.399	1.395	1.381	1.390
C (2)–C (3)	1.372	1.395	1.385	1.400
C (3)–C (4)	1.378	1.374	1.385	1.400
C (4)–C (5)	1.388	1.379	1.381	1.390
C (5)–N	1.336	1.326	1.335	1.340
C (1)–C (6)	1.507	1.500	1.525	
C (5)–C (7)	1.511	1.508	1.525	
C (6)–O (1)	1.217	1.240	1.245	
C (6)–O (2)	1.288	1.256	1.258	
C (7)–O (3)	1.181	1.245	1.258	
C (7)–O (4)	1.315	1.254	1.245	
Bond angle				
C (5)–N –C (1)	116.8°	119.6°	118.8°	116.7°
N –C (1)–C (2)	123.4	122.4	122.4	124.0
C (1)–C (2)–C (3)	118.9	116.9	118.7	118.6
C (2)–C (3)–C (4)	118.2	120.1	118.9	118.1
C (3)–C (4)–C (5)	119.4	119.0	118.7	118.6
C (4)–C (5)–N	123.3	121.6	122.4	124.0
N –C (1)–C (6)	118.2	114.9	115.4	
C (2)–C (1)–C (6)	118.4	122.7	112.4	
N –C (5)–C (7)	115.3	114.8	115.4	
C (4)–C (5)–C (7)	121.4	123.3	122.4	
O (1)–C (6)–C (1)	119.2	117.6	117.4	
O (2)–C (6)–C (1)	116.3	116.9	117.2	
O (1)–C (6)–O (2)	124.4	125.4	125.5	
O (3)–C (7)–C (5)	124.4	116.4	117.2	
O (4)–C (7)–C (5)	110.4	118.1	117.4	
O (3)–C (7)–O (4)	124.4	125.5	125.3	

(a) Dipicolinic acid (This study).
(b) Calcium dipicolinate (G. Strahs and R. E. Dickerson, *Acta. Crystallogr.*, **B24**, 571 (1968)).
(c) Strontium dipicolinate (K.J. Palmer, R.Y. Wong, and J. C. Lewis, *ibid.*, **B28**, 233 (1972)).
(d) Pyridine (B. Bak, L. H. Nygaard, and J. R. Andersen, *J. Mol. Spectrosc.*, **2**, 361 (1958)).

also agrees considerably well in dimensions with those of the salts of calcium and strontium.

The C(1)–N–C(5) bond angel is 116.8°; this means that the protonation did not occur on the nitrogen atom of the pyridine ring. The lengths of two C–C bonds joining the ring to the carboxyl groups are equal within the limits of experimental error; the average value is 1.509 Å, which is quite normal. The two C–O bond lengths in each carboxyl group are clearly different from each other. The bonds between the carbon and carbonyl oxygen atoms, C(6)–O(1) and C(7)–O(3), are shorter than those between the carbon and hydroxyl oxygen atoms, C(6)–O(2) and C(7)–O(4), by an average value of 0.108 Å. This finding also supports the fact that the hydrogen atoms of dipicolinic acid are definitely associated with the hydroxyl oxygen atoms. In both carboxyl groups, the C–C–O angles associated with the shorter C–O bonds are larger than those associated with longer C–O bonds, as is usually observed in carboxylic acids. There is a very simple relation between the C–O bond length and the C–C–O bond angle. This relation is $1/d=e\cdot\sin\theta+f$, where d is the C–O bond length, where θ is the C–C–O bond angle shown as follows;



and where e and f are constants. This relation is shown in Fig. 5. In spite of the simplicity of this equation, there is a good correlation between the experimental values.

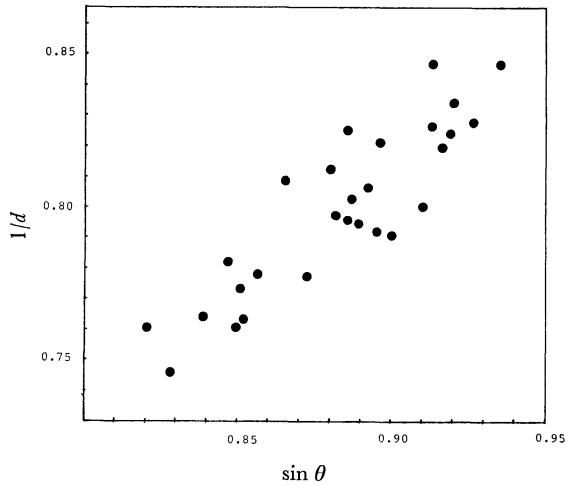


Fig. 5. The relation between the C–O bond lengths and C–C–O bond angles in carboxyl groups. The plotted compounds are dipicolinic acid, dinicotinic acid, quinolinic acid, cinchomeronic acid, calcium dipicolinate, strontium dipicolinate and oxalic acid.

The differences between the N–C(1)–C(6) and N–C(5)–C(7) bond angles, and between the C(2)–C(1)–C(6) and C(4)–C(5)–C(7) bond angles, are 3.1° and −3.2° respectively. These differences are significant, judging from their estimated standard deviations, and were not observed in calcium dipicolinate[4] and strontium dipicolinate.[5] This means that such differences depend on the orientation of the carboxyl groups and on the formation of hydrogen bonds. One carboxyl group (C(6)O(1)O(2)H(4)) is twisted by 0.8° out of the plane of the pyridine ring, while the other (C(7)O(3)O(4)H(5)) is twisted by 0.5° in the directions shown in Fig. 3.

Molecular Arrangement and Hydrogen-bond System. The crystal structure is shown in Figs. 6, 7, and 8. The distances and angles of hydrogen bonds are listed in Table 7. The dipicolinic acid and water molecules are arranged in layers closely parallel to the (0 0 1) plane, except the one hydrogen atom of the water molecule, and lie on the planes at $z=1/8$, 3/8, 5/8, and 7/8. These planes have a spacing of 1.704 Å. The best plane through the non-hydrogen atoms of a dipicolinic acid and a water molecule is calculated by the least-squares analysis to be:

$$0.0343X + 0.0171Y + 0.9993Z = 1.1129.$$

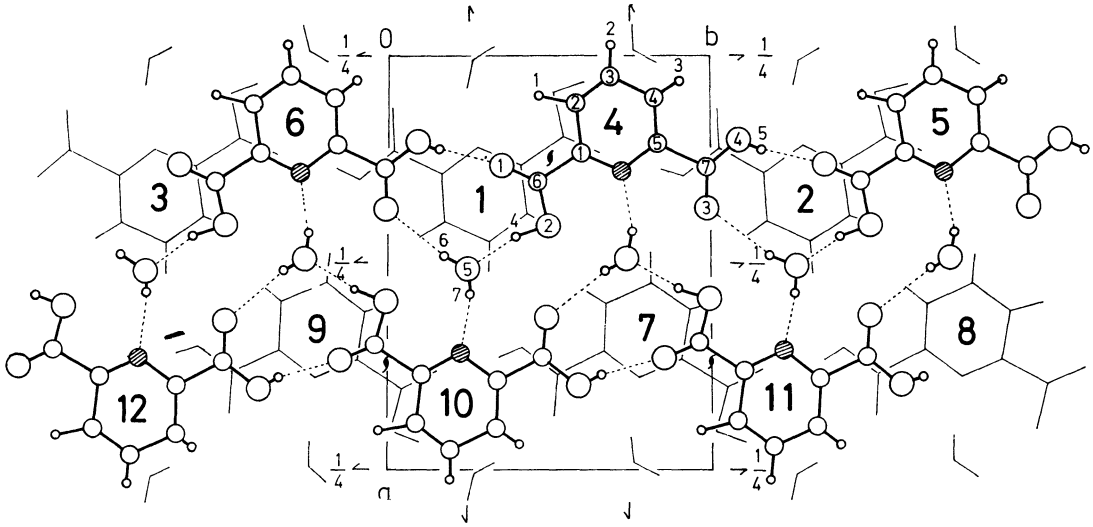


Fig. 6. A view of the crystal structure along the *c* axis, showing the relative orientation of the molecules in two adjacent layers parallel to the (0 0 1) plane. The hydrogen bonds are shown by broken lines.

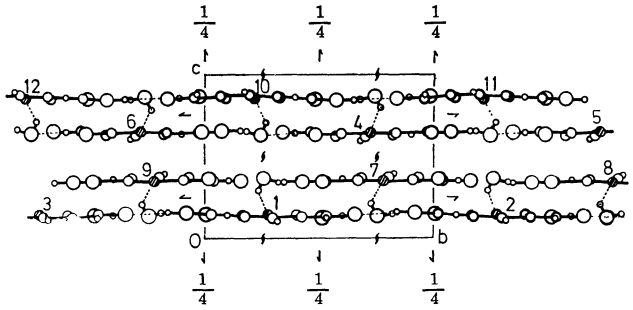


Fig. 7. A view of the crystal structure down the *a* axis. The hydrogen bonds are shown by broken lines.

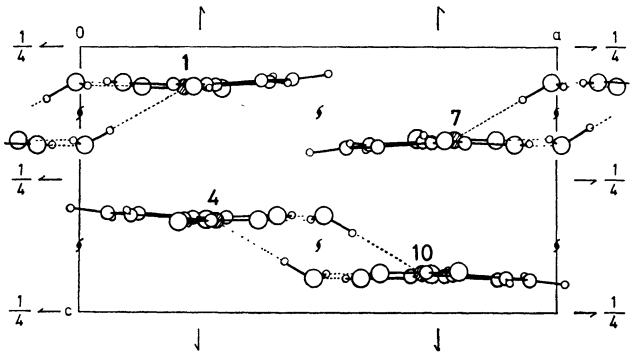


Fig. 8. A view of the crystal structure down the *b* axis. The hydrogen bonds are shown by broken lines.

The dihedral angle which it makes with the (0 0 1) plane is 2.1°. Figures 7 and 8 show the view parallel to the (0 0 1) plane, while Fig. 6 shows a view normal to the (0 0 1) plane, which illustrates the relative orientations of the molecules in two neighboring layers. The upper layer of the molecules drawn with heavy lines in this figure involves the molecules on the planes at $z=5/8$ and 7/8. In Figs. 6, 7, and 8, the same numerals designate the same molecules. The symmetry codes involving molecules which have these numbers are shown in Table 6.

Each molecule on the same plane is joined, through three hydrogen bonds, O(4)–H(5)···O(1), O(2)–H(4)···O(5), and O(5)–H(6)···O(3), with two neighboring molecules, and each forms an infinite chain along the *b* axis. In the O(4)–H(5)···O(1) hydrogen bond,

TABLE 7. HYDROGEN BOND DISTANCES (Å) AND ANGLES (DEGREE)

O——H·····X	Symmetry	O···X	e.s.d.	O–H	e.s.d.	H···X	e.s.d.	Angle	e.s.d.
O (2)–H (4)···O (5)	(4, 4, 4)	2.561	0.005	0.88	0.05	1.70	0.05	165	5
O (4)–H (5)···O (1)	(4, 4, 5)	2.584	0.007	0.75	0.05	1.85	0.05	164	5
O (5)–H (6)···O (3)	(4, 4, 6)	2.920	0.006	0.69	0.04	2.25	0.04	164	5
O (5)–H (7)···N	(4, 4, 10)	2.941	0.005	0.79	0.06	2.17	0.06	163	6

X——O·····H	Symmetry	Angle	e.s.d.	X——Y·····O	Symmetry	Angle	e.s.d.
C (1)–N ···H (7)	(4, 4, 11)	123	2	C (1)–N ···O (5)	(4, 4, 11)	118.2	0.3
C (5)–N ···H (7)	(4, 4, 11)	114	2	C (5)–N ···O (5)	(4, 4, 11)	117.8	0.3
C (6)–O (1)···H (5)	(4, 4, 6)	166	2	C (6)–O (1)···O (4)	(4, 4, 6)	170.6	0.4
C (7)–O (3)···H (6)	(4, 4, 5)	136	1	C (7)–O (3)···O (5)	(4, 4, 5)	132.5	0.4
H (6)–O (5)···H (4)	(4, 4, 4)	122	4	N·····O (5)···O (2)	(10, 4, 4)	118.4	0.2
H (7)–O (5)···H (4)	(4, 4, 4)	108	4	O (3)···O (5)···O (2)	(6, 4, 4)	115.8	0.2

Symmetry
1 = (x, y, z)
2 = $(x, 1+y, z)$
3 = $(x, -1+y, z)$
4 = $(1/2-x, 1-y, 1/2+z)$
5 = $(1/2-x, 2-y, 1/2+z)$
6 = $(1/2-x, -y, 1/2+z)$
7 = $(1-x, 1/2+y, 1/2-z)$
8 = $(1-x, 3/2+y, 1/2-z)$
9 = $(1-x, -1/2+y, 1/2-z)$
10 = $(1/2+x, 1/2-y, 1-z)$
11 = $(1/2+x, 3/2-y, 1-z)$
12 = $(1/2+x, -1/2-y, 1-z)$

the C(6)–O(1)···H(5) and C(6)–O(1)···O(4) hydrogen bonding angles are 166° and 170.6° respectively. These values indicate that the bisector of the lone pairs in the carbonyl oxygen atom O(1) is directed toward a hydrogen-bond donor group. On the other hand, the C(7)–O(3)···H(6) and C(7)–O(3)···O(5) hydrogen bonding angles are 136° and 132.5° in the O(5)–H(6)···O(3) hydrogen bond. In this case, one of the lone pairs in the carbonyl oxygen atom O(3) is directed toward a hydrogen-bond donor group, as is usually observed in hydrogen bonds.

These two chains on the planes at $z=1/8$ and 3/8 are linked together by the O–H···N hydrogen bond between the water and the pyridine ring, and form a double chain along the *b* axis. The angle between the N···H(7) vector of the hydrogen bond and the plane of the pyridine ring is 28°, and the distances between N and H(7) and between N and O(5) are 2.07 and 2.941 Å respectively. Since the two carboxyl groups in α-positions prevent the formation of the O–H···N hydrogen bond which is parallel to the pyridine plane, the donor group of the hydrogen bond may deviate from the pyridine plane. In spite of such a steric hindrance and the presence of some other acceptors of the hydrogen bond, the O–H···N hydrogen bond is formed in this crystal. This suggests that the O–H···N hydrogen bond is more energetically favored than the O–H···O hydrogen bond in solids. The hydrogen-bonding system is also the same in the two chains on planes at $z=5/8$ and 7/8. These double chains are not joined by the hydrogen bond, but only by the van der Waals forces. Thus, the hydrogen-bond system in dipicolinic acid monohydrate plays an important role in connecting the molecules along the *b* axis.

The relation between the thermal diffuse scattering and the crystal structure can be explained on the basis of this hydrogen-bond system. There is an anisotropy of the bonding forces joining the molecules in the crystal. The molecules are linked by a strong hydrogen bond along the double chains (along the *b* axis in the crystal), but only the weak van der Waals forces act between chains (that is, perpendicular to the *b* axis). The nature of the bonding forces suggests that the vibrations are almost out-of-phase among different chains (almost an independent motion of one chain with respect to the others), but there should be a strong interaction in the motion of the molecules along the same chain. Therefore, the continuous thermal diffuse scattering appears along the directions of the a^* and c^* axes. Similar patterns were also observed in the crystals with molecules joined in the chain by hydrogen bonds.[12]

It will be of interest to compare the crystal structure of the present compound with that of isophthalic acid,[13] since they have similar frameworks and isoelectronic structures. The crystals of isophthalic acid which were recrystallized from the aqueous solution are not hydrates, and the molecules of isophthalic acid are linked together by hydrogen bonds between carboxyl groups. The reason for this difference between the crystal structures of these two compounds is the presence of a nitrogen atom in dipicolinic acid and the O–H···N hydrogen-bond formation with the aid of a water molecule.

Computer Programs. All the calculations were performed on a FACOM 270-30 computer at the Computer Center of Osaka City University using the following programs: RSLC-3 (cell constant),[14] RSSFR-3 (Fourier synthesis),[15] HBLS-IV (block-diagonal least-squares refinement),[16] DAPH (bond length, bond angle, and least-squares plane,[17] SCALE (film factor, Lp, and layer scaling),[18] TE-I (thermal ellipsoid),[19] PHASE-I, II, III (symbolic addition),[20] and CNINDO (CNDO and INDO calculations).[11]

The authors wish to express their thanks to Dr. K. Nishimoto of this faculty for his useful advice on the CNDO calculations.

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17) T. Ashida, *ibid.*, p. 76.
18) H. Yoshioka, K. Hirotsu, and F. Takusagawa, unpublished work.
19) F. Takusagawa, unpublished work.
20) K. Nakatsu and K. Hirotsu, unpublished work.