The Crystal Structure of Cinchomeronic Acid

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The crystal structure of cinchomeronic acid (3,4-pyridinedicarboxylic acid) has been determined by the method of X-ray diffraction. The crystals are orthorhombic, with a space group of $P2_12_12_1$, and with cell dimensions of $a=11.211$, $b=11.206$, and $c=5.285$ Å. The structure was determined by the method of symbolic addition. The final R value was 5.90% for 828 observed reflections. The molecule takes the form of a zwitter ion in the crystal. The pyridine ring has, approximately, the C_{2v} symmetry. One carboxyl group consists of C=O and C–O(H) groups, while the other consists of two C···O groups. These carboxyl groups twist out of the plane of a pyridine ring by 39.6° and 73.0° respectively. The hydrogen bonds are in the forms of two spirals around the two-fold screw axes parallel to the c axis, thus linking the molecules three-dimensionally. There are four molecules per turn of the spiral along the c axis. The carbonyl oxygen atom O(2) is free from the hydrogen bond, while the nitrogen atom N(1) in the pyridine ring participates in it. The relations between the C–N–C bond angle of the pyridine ring and the N···H distance, and also between the net charge on the nitrogen atom calculated by the "complete neglect of differential overlap" (CNDO) method and the O···N distance for a hydrogen bond are discussed in connection with five pyridine-carboxylic acids.

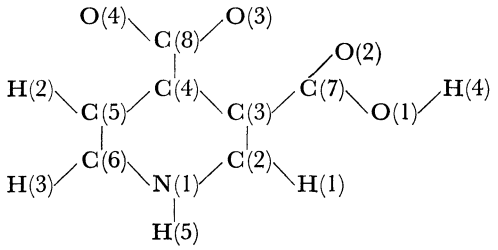
This work is a part of series of O–H···N hydrogen bonding studies by means of X-ray crystal structure analyses of some carboxylic acids based on a pyridine ring. In the course of this study, some interesting features have been revealed in connection with the form of a molecule as well as with the type of hydrogen-bond formation. Thus, the nicotinic acid[1] and dipicolinic acid[2] molecules took a neutral form, while the quinolinic acid[3] molecule took the form of a zwitter ion. The dinicotinic acid[4] molecule was intermediate between the above two forms. Such a problem does not occur in carboxylic acids based on a benzene ring, since they do not involve a nitrogen atom, which can also take part in a hydrogen bond. Moreover, the relation among the molecular forms (neutral or intermediate or zwitter ion), the positions of the substituted carboxyl groups and the hydrogen-bonding system has not been established in the crystal structures studied hitherto. In this sense, it seemed that it would be of interest to elucidate the effect of a nitrogen atom in a pyridine ring on the hydrogen-bond formation in solids. The cinchomeronic acid molecule in the present study can take three forms—neutral, intermediate and zwitter ions, and it has the same framework and isoelectronic structure as phthalic acid[5] and quinolinic acid. It is also of interest to study the intramolecular hydrogen bond between adjacent carboxyl groups, because it has already been found in the crystals of quinolinic acid, but not in those of phthalic acid.

Experimental

The crystals were obtained in the form of colorless prisms by recrystallization from an aqueous solution. Weissenberg photographs showed the crystal to be orthorhombic, with the space group $P2_12_12_1$. The unit cell dimensions were measured from zero-layer Weissenberg photographs, which were calibrated with superimposed Al powder lines. The crystal data are given in Table 1. Using a spherically shaped crystal with an average diameter of 0.4 mm, the intensity data were collected for the 0—5 layers around the c axis and for the 0—2 layers around the b axis by the use of a multiple-film equi-inclination integrating Weissenberg technique, with Cu$K\alpha$ radiation. The intensities were estimated visually by comparison with an intensity standard. Of the possible 922 reflections within the Cu$K\alpha$ sphere, 848 independent reflections were measured; 20 were too weak to be observed. No absorption and extinction corrections were applied.

TABLE 1. CRYSTAL DATA FOR CINCHOMERONIC ACID

Molecular formula	$C_7H_5NO_4$
Molecular weight	167.12
Crystal size	~0.4×0.4×0.4 mm
Crystal system	Orthorhombic
Space group	$P2_12_12_1$
Cell dimensions;	
a	11.211±0.006 Å
b	11.206±0.004
c	5.285±0.003
V	664.0±0.6 Å^3
Z	4
Density(calculated)	1.672 g/cm^3
Density(observed)	1.65
Radiation	Cu$K\alpha$ ($\lambda=1.5418$ Å)
Linear absorption coefficient	13.95 cm^{-1}
Number of independent reflections	848
Atom numbering	



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Structure Determination and Refinement

The crystal structure was solved easily by the symbolic addition method. The first postulated structure gave an R value of 41%; this decreased to 17% after three cycles of least-squares refinements with individual isotropic thermal parameters.

Anisotropic thermal parameters were then introduced, and the block-diagonal least-squares refinement was

TABLE 2. THE OBSERVED AND CALCULATED STRUCTURE FACTORS

F_o, F_c and DF have been multiplied by 10.

The unobserved reflection is indicated by an asterisk. The reflection with $|F_o - F_c| / |F_o|$ larger than 0.3 is indicated by a plus sign.

K	FO	FC	DF	K	FO	FC	DF	K	FO	FC	DF	K	FO	FC	DF	K	FO	FC	DF	K	FO	FC	DF	K	FO	FC	DF
H,L= 0	0			3	16	16	0	6	81	86	-5	1	27	28	0	3	175	171	3	4	22	26	-4	1	101	106	-4
2	291	280	10	4	141	152	-10	7	110	112	-1	2	105	106	0	4	152	149	3	5	58	57	0	2	200	192	7
4	485	490	-5	5	170	167	2	8	41	49	-7	3	21	18	3	5	203	211	-7	6	33	28	4	3	99	101	-1
6	84	87	-2	6	99	100	-1	9	55	58	-2	4	13	15	-1	6	225	221	4	7	40	36	3	4	42	42	0
8	316	312	3	7	55	54	1	10	36	40	-4	5	53	59	-5	7	45	52	-7	8*	0	3	-3	5	81	81	0
10	17	17	0	8	97	90	7	11	7	9	-1	6	54	56	-1	8	36	42	-5	9	9	10	-1	6	65	67	-1
12	55	61	-5	9	48	46	2	12	27	29	-2	7	109	98	11	9	80	82	-1	10	61	55	5	7	23	24	-1
14	12	12	0	10	81	74	6	13	15	16	-1	8	32	32	0	10	116	112	3	H,L= 10		2		8	64	65	0
H,L= 1	0			11*	0	1	-1	14	26	23	3	9	37	36	0	11	33	32	0	0	60	62	-2	9	29	26	2
1	118	121	-3	12	18	22	-4	H,L= 2		1		10	46	46	0	12	39	40	0	1	132	122	9	10	51	51	0
2	74	77	-2	H,L= 8		0		0	413	389	24	11	42	38	3	13	60	54	6	2	17	19	-1	11	5	5	0
3	47	60	-12	0	137	137	0	1	818	757	61	H,L= 9		1		H,L= 3		2		3	37	40	-3	12	18	13	4
4	599	583	15	1	60	66	-5	2	471	465	5	0	24	26	-1	0	5	7	-1	4	47	51	-4	H,L= 5		3	
5	29	33	-3	2	32	33	-1	3	275	271	4	1	84	82	2	1	256	246	10	5	31	31	0	0	15	17	-2
6	97	106	-8	3	13	13	0	4	118	120	-2	2	82	83	-1	2	301	280	21	6	54	50	4	1	86	85	1
7	157	146	11	4*	0	4	-4	5	122	129	-7	3	152	147	4	3	311	297	14	7	75	71	3	2	62	61	0
8*	0	3	-3	5	114	118	-4	6	31	37	-5	4	82	86	-4	4	46	48	-2	8	19	20	-1	3	41	44	-3
9	21	22	0	6	57	54	2	7	191	193	-2	5	40	45	-4	5	135	134	1	9	23	23	0	4	54	59	-5
10	12	15	-3	7	28	29	-1	8	77	78	-1	6	128	119	8	6	38	43	-5	H,L= 11		2		5	100	94	5
11	8	9	-1	8	36	34	1	9	67	69	-1	7	24	25	-1	7	248	240	8	0	22	24	-1	6	32	30	1
12	13	13	0	9	53	49	3	10	83	82	1	8	5	5	0	8	17	20	-2	1	24	29	-4	7	54	56	-1
13	51	54	-2	10	22	20	2	11	83	81	2	9	42	43	0	9	39	41	-2	2	55	54	0	8	57	58	-1
14	20	23	-2	11	24	27	-2	12	14	13	0	10	38	39	0	10	49	48	0	3	29	28	1	9	82	74	8
H,L= 2	0			H,L= 9		0		13	20	21	0	H,L= 10		1		11	22	22	0	4	46	48	-1	10	27	25	2
0	280	277	2	1	93	88	4	14	34	35	0	0	128	118	10	12	19	22	-2	5	32	30	2	11	15	11	4
1	342	334	7	2	18	21	-2	H,L= 3		1		1	154	153	0	13	41	35	5	6*	0	2	-2	H,L= 6		3	
2	508	550	-41	3	31	27	4	0	164	155	8	2	70	73	-2	H,L= 4		2		7	41	42	0	0	63	62	0
3	256	263	-6	4	178	167	10	1	377	346	30	3	30	33	-3	0	333	319	14	8	7	9	-2	1	114	120	-6
4	27	33	-6	5	28	27	0	2	249	250	0	4	27	33	-5	1	83	85	-2	H,L= 12		2		2	101	100	1
5	23	25	-1	6	22	19	3	3	487	460	26	5	50	54	-4	2	204	202	2	0	64	59	4	3	213	207	6
6	161	165	-4	7	94	83	10	4	36	39	-3	6	26	29	-3	3	97	104	-6	1	11	12	-1	4	137	143	-6
7	95	97	-1	8	50	43	6	5	144	155	-10	7	95	81	13	4	119	120	0	2	18	20	-2	5	10	9	0
8	106	110	-4	9	55	48	6	6	159	163	-4	8	24	25	0	5	136	138	-1	3	50	49	1	6	14	17	-2
9	59	61	-1	10	37	33	4	7	89	104	-14	9	21	19	2	6	49	52	-2	4	10	8	2	7	12	10	2
10	53	49	3	11	69	63	6	8	54	60	-6	10	22	19	2	7	103	103	0	5	38	41	-2	8	53	53	0
11*	0	0	0	H,L= 10		0		9	82	84	-1	H,L= 11		1		8	98	103	-5	6	22	20	2	9*	0	5	-5
12	82	84	-1	0	39	43	-3	10	57	59	-1	0	43	40	2	9	55	61	-6	H,L= 13		2		10	27	23	3
13	27	30	-3	1	84	83	0	11	50	48	2	1	40	41	-1	10	50	49	0	0+	2	1	1	11	32	28	4
14	11	13	-2	2*	0	4	-4	12	37	37	0	2	49	46	2	11	32	27	4	1	8	11	-2	H,L= 7		3	
H,L= 3	0			3	95	94	0	13	18	19	0	3	48	45	2	12	21	24	-2	2	15	15	0	0	178	182	-4
1	76	81	-5	4	37	39	-2	H,L= 4		1		4	7	8	0	13	25	23	1	3	27	27	0	1	90	92	-2
2+	11	14	-3	5	31	30	0	0	19	21	-2	5	22	22	0	H,L= 5		2		4	46	48	-2	2	66	65	0
3	123	119	4	6	73	67	6	1	149	158	-8	6	17	21	-3	0	56	62	-5	H,L= 0		3		3	60	62	-1
4	386	406	-20	7*	0	2	-2	2	518	502	15	7	30	29	0	1	222	218	4	0+	0	0	0	4	92	88	4
5	280	274	6	8	20	22	-1	3	210	207	3	8	14	13	0	2	94	104	-9	1	137	147	-9	5	100	105	-5
6	133	118	15	9	26	22	4	4	109	104	4	9*	0	17	-17	3	87	92	-5	2	129	124	5	6	30	27	3
7	166	156	9	10	74	61	13	5	21	22	0	H,L= 12		1		4	122	116	5	3	65	64	0	7	26	26	0
8	140	144	-3	H,L= 11		0		6	99	115	-15	0	20	19	0	5	85	85	0	4	142	137	4	8	72	70	2
9	90	91	0	1	58	56	2	7	84	84	0	1	87	89	-1	6	24	27	-2	5	124	117	6	9	13	11	1
10*	0	4	-4	2	106	102	3	8	114	127	-12	2	14	17	-2	7	20	21	-1	6	264	254	9	10	7	8	0
11	2	2	0	3	21	23	-2	9	48	51	-2	3	47	51	-3	8	86	83	2	7	104	102	1	H,L= 8		3	
12	26	27	0	4	134	128	6	10	112	108	3	4	30	30	0	9	120	109	10	8	68	66	1	0	60	64	-4
13	13	14	-1	5	31	28	3	11	41	45	-3	5	22	22	0	10	41	40	1	9	91	90	1	1	116	119	-3
14	22	24	-2	6*	0	0	0	12	9	10	-1	6	32	32	0	11	18	15	2	10	34	31	3	2	54	56	-2
H,L= 4	0			7*	0	1	-1	13	37	34	3	7	33	27	5	12	42	41	0	11	38	34	4	3	28	34	-6
0	96	93	3	8+	7	4	3	H,L= 5		1		H,L= 13		1		H,L= 6		2		12	11	11	0	4	96	91	5
1	65	73	-7	9	35	32	2	0	28	30	-2	0	58	52	5	0	148	157	-8	H,L= 1		3		5	79	81	-1
2	28	28	0	H,L= 12		0		1	91	94	-3	1	15	19	-4	1	22	16	5	0	212	239	-27	6	58	55	3
3	45	50	-4	0	120	114	6	2	161	172	-10	2	10	11	-1	2	134	137	-3	1	94	103	-8	7	41	43	-1
4	13	14	-1	1	30	31	0	3	47	52	-4	3	56	51	4	3	182	199	-16	2	44	40	4	8	36	36	0
5	60	58	2	2	60	58	1	4	158	160	-2	4	5	5	0	4	88	93	-4	3	155	157	-2	9	28	29	0
6	92	96	-4	3	96	92	4	5	138	139	0	5	11	11	0	5	46	52	-6	4	59	57	1	10	25	29	-4
7	74	68	5	4	12	11	1	6	125	135	-10	H,L= 14		1		6	96	97	0	5	90	96	-5	H,L= 9		3	
8	35	41	-6	5	17	16	1	7	79	84	-5	0	5	5	0	7	38	40	-1	6	120	129	-8	0	66	71	-4
9	37	39	-2	6	52	47	5	8	81	84	-2	1	10	13	-2	8	38	38	0	7	107	111	-4	1	86	77	8
10	29	28	1	7	27	29	-1	9	20	23	-3	2	18	20	-2	9	41	42	-1	8	128	131	-2	2	61	58	3
11	28	28	0	H,L= 13		0		10	39	43	-4	H,L= 0		2		10	11	14	-2	9	99	105	-5	3	92	96	-3
12	7	6	0	1	13	9	3	11	26	27	0	0+	37	60	-23	11	41	39	1	10	101	95	5	4	48	48	0
13	30	36	-5	2	45	43	2	12+	10	13	-3	1+	10	17	-6	12	35	28	6	11	82	78	3	5	27	27	0
H,L= 5	0			3	6	4	1	13	38	34	4	2	293	303	-9	H,L= 7		2		12	23	20	3	6	52	53	0
1	27	25	2	4	56	58	-1	H,L= 6		1		3	255	237	17	0	67	72	-4	H,L= 2		3		7	29	25	4
2	210	191	18	5	9	7	2	0	118	126	-8	4	162	144	17	1	76	87	-11	0	211	218	-6	8	31	29	1
3	22	29	-6	6	7	7	0	1	170	179	-8	5+	10	6	4	2	67	73	-5	1	190	184	5	9	18	20	-1
4	133	127	5	H,L= 14		0		2	90	104	-14	6	274	258	15	3	37	35	2	2	74	66	8	H,L= 10		3	
5	138	142	-3	0	1	1	0	3	40	43	-2	7	37	36	1	4	21	21	0	3	103	95	8	0	22	25	-2
6	38	39	0	1	10	10	0	4	84	92	-7	8	11	9	1	5	69	71	-2	4	223	224	0	1	77	70	6
7	134	141	-6	2	29	27	1	5	91	96	-5	9	35	38	-2	6	83	83	0	5	93	102	-8	2	44	44	0
8	161	153	7	H,L= 0		1		6	61	70	-9	10	35	35	0	7	22	21	1	6	74	71	2	3	36	35	0
9	73	78	-4	0+	1	0	1	7	33	35	-1	11	155	142	12	8	21	19	2	7	112	119	-6	4	90	76	13
10	36	39	-3	1	199	184	15	8	89	89	0	12	75	69	5	9	29	27	1	8	75	76	-1	5	26	25	0
11	18	23	-4	2	491	452	39	9	103	103	0	13	14	15	-1	10	63	58	5	9	20	21	0	6	31	31	0
12	33	33	0	3	263	248	14	10	31	32	0	H,L= 1		2		11+	10	13	-3	10	42	42	0	7	32	30	2
13	41	42	-1	4	410	398	12	11	17	17	0	0	89	97	-8	H,L= 8		2		11	16	13	2	8	7	6	1
H,L= 6	0			5	67	76	-9	12	3	3	0	1	344	323	20	0	219	214	4	12	51	49	1	H,L= 11		3	
0	252	242	10	6	127	126	0	H,L= 7		1		2	240	218	21	1	119	120	-1	H,L= 3		3		0	82	74	8
1	289	282	7	7	77	91	-13	0	20	18	1	3	185	178	7	2	95	98	-2	0	119	129	-10	1	23	25	-1
2	45	48	-2	8	90	94	-3	1	51	61	-9	4	242	249	-7	3	78	76	1	1	111	112	-1	2	30	27	3
3	230	221	9	9	13	9	4	2	136	144	-8	5	98	98	0	4	73	81	-7	2	107	100	6	3	10	10	0
4	94	88	6	10	118	126	-8	3	123	136	-13	6	47	44	3	5	108	110	-1	3	154	159	-5	4	56	50	5
5*	0	5	-5	11	92	93	0	4	52	54	-1	7	93	96	-3	6	132	124	7	4	49	51	-1	5	21	22	0
6	54	57	-2	12	29	32	-3	5	46	53	-6	8	94	97	-3	7	27	32	-5	5	59	59	0	6	30	25	5
7	77	72	4	13	46	49	-2	6	127	122	4	9	52	56	-4	8*	0	4	-4	6	57	59	-1	H,L= 12		3	
8	67	67	0	14	35	35	0	7	118	120	-2	10	107	116	-8	9	2	3	0	7	102	104	-1	0	21	22	-1
9	141	156	-14	H,L= 1		1		8	26	29	-2	11	22	24	-1	10	24	19	4	8	50	50	0	1	19	19	0
10	52	52	0	0	208	203	5	9	87	87	0	12	31	31	0	11	7	5	2	9	70	67	2	2	26	25	1
11	33	33	0	1	377	347	30	10	58	58	0	13	7	8	-1	H,L= 9		2		10+	18	23	-5	3	29	21	8
12	52	51	0	2	171	196	-25	11	61	55	6	H,L= 2		2		0	145	140	4	11	31	29	1	4	30	26	4
H,L= 7	0			3	627	577	49	12	24	23	1	0	6	6	0	1	62	69	-7	12	51	48	2	H,L= 13		3	
1	270	257	13	4	31	36	-4	H,L= 8		1		1	244	263	-18	2	116	119	-3	H,L= 4		3		0*	0	7	-7
2	70	70	0	5	290	284	6	0	19	19	0	2	85	87	-1	3	20	22	-2	0	101	111	-9	H,L= 0		4	

Table 2 (Continued)

K	FO	FC	DF	K	FO	FC	DF	K	FO	FC	DF	K	FO	FC	DF	K	FO	FC	DF	K	FO	FC	DF	K	FO	FC	DF
0	162	179	-17	8	21	24	-2	4	36	36	0	4	40	43	-3	7*	10	7	3	8	35	34	1	2	16	17	0
1	62	71	-8	9	22	28	-5	5	24	20	3	5	26	29	-2	8	4	5	-1	9	18	19	0	3	17	21	-4
2	28	36	-8	10	11	12	0	6	42	43	-1	6	44	37	6	9*	0	3	-3	H+L=	4	5		4	13	12	1
3	168	153	14	11	14	14	0	7	70	69	1	7	25	25	0	H+L=	1	5		0	39	36	2	5	14	14	0
4	122	106	16	H+L=	3	4		8*	0	3	-3	8	25	32	-7	0	88	88	0	1	75	77	-2	6	65	64	1
5	153	167	-14	0	13	15	-2	9	23	23	0	H+L=	4	4		1	109	103	6	2	110	100	9	H+L=	8	5	
6	147	138	9	1	88	91	-2	10	62	57	4	0	14	16	-2	2	70	53	17	3	76	72	3	0	75	76	-1
7	20	17	2	2	70	72	-1	H+L=	6	4		1	33	39	-5	3	23	19	3	4	42	45	-3	1	29	30	0
8	44	43	1	3	89	85	4	0	202	205	-3	2	26	30	-3	4	15	14	1	5	29	35	-6	2	39	43	-3
9	30	33	-2	4	53	54	-1	1	63	60	3	3	27	29	-2	5	102	96	5	6	29	27	2	3	20	21	-1
10	52	50	1	5	94	96	-2	2	35	34	0	4	43	43	0	6	42	39	2	7	65	69	-4	4	16	20	-3
11	9	11	-1	6	58	62	-3	3	102	102	0	5+	11	14	-3	7	36	34	2	8	22	20	2	5	24	26	-1
H+L=	1	4		7	122	114	8	4	54	63	-9	6	15	18	-3	8	17	14	3	H+L=	5	5		H+L=	9	5	
0	106	114	-7	8	17	16	0	5	13	13	0	7	14	15	-1	9	36	38	-1	0	9	10	-1	0	48	53	-4
1	110	104	5	9	32	28	3	6	76	78	-2	H+L=	10	4		H+L=	2	5		1	28	26	1	1	22	23	0
2	119	109	10	10	55	52	2	7	36	36	0	0	9	10	0	0	33	29	4	2	37	40	-2	2	31	37	-6
3	74	70	4	11	20	23	-3	8	46	41	4	1	33	33	0	1*	23	14	9	3	76	84	-8	3	29	28	1
4	20	20	0	H+L=	4	4		9	50	46	4	2	12	11	1	2	89	79	9	4	14	13	1				
5	189	156	33	0	29	30	0	H+L=	7	4		3	50	54	-4	3	131	129	1	5	2	2	0				
6	71	66	4	1	68	78	-9	0	104	110	-5	4	27	27	0	4	115	113	2	6	18	20	-2				
7	98	97	1	2	105	113	-8	1	32	34	-1	5	39	43	-3	5	52	55	-3	7	27	27	0				
8	19	16	2	3	140	124	15	2	67	72	-5	H+L=	11	4		6	33	34	0	8	36	40	-4				
9	38	44	-6	4	128	121	6	3	26	30	-3	0*	0	0	0	7	17	20	-2	H+L=	6	5					
10	34	36	-1	5	41	40	1	4	166	154	12	1	38	43	-4	8	37	32	5	0	48	48	0				
11	15	16	0	6	90	83	7	5	37	38	0	2	28	32	-4	9	26	23	2	1	47	51	-3				
H+L=	2	4		7	37	36	1	6	39	41	-1	3	16	17	-1	H+L=	3	5		2	30	34	-4				
0+	5	0	5	8	19	18	1	7	23	25	-1	H+L=	0	5		0	69	72	-3	3	25	30	-5				
1	47	50	-2	9	29	29	0	8	30	28	2	0*	0	0	0	1	106	102	4	4	39	41	-2				
2	156	132	23	10	20	15	5	9	26	27	-1	1	66	63	3	2	20	19	0	5	5	3	1				
3	45	45	0	H+L=	5	4		H+L=	8	4		2	114	102	11	3	109	97	12	6	9	11	-1				
4	37	36	0	0	41	47	-6	0	28	33	-5	3	21	16	4	4	141	138	3	7+	16	24	-7				
5	105	111	-6	1	97	99	-1	1	48	50	-1	4	38	39	-1	5	36	40	-4	H+L=	7	5					
6	37	44	-7	2	156	146	10	2	28	31	-2	5	112	112	0	6	51	63	-12	0	29	26	2				
7	65	57	7	3	98	97	1	3	47	60	-12	6	16	19	-3	7	35	34	0	1+	7	4	2				

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 10^4. For the hydrogen atoms, the values listed are isotropic thermal parameters B(Å^2).

Atom	x	y	z	B
N(1)	2012(3)	1974(3)	5763(6)	—
C(2)	2673(3)	1531(3)	7646(7)	—
C(3)	3608(3)	2173(3)	8622(6)	—
C(4)	3825(3)	3324(3)	7660(6)	—
C(5)	3111(3)	3764(3)	5762(7)	—
C(6)	2208(3)	3067(4)	4776(8)	—
C(7)	4465(3)	1601(3)	10438(7)	—
C(8)	4798(3)	4117(3)	8733(7)	—
O(1)	3944(2)	917(2)	12118(5)	—
O(2)	5521(2)	1762(3)	10265(6)	—
O(3)	5699(2)	4317(2)	7423(5)	—
O(4)	4562(3)	4551(3)	10835(6)	—
H(1)	251(3)	72(3)	826(7)	3.1(0.9)
H(2)	326(3)	457(4)	508(9)	4.2(1.0)
H(3)	161(4)	334(4)	336(10)	5.1(1.1)
H(4)	459(3)	43(3)	1259(8)	3.6(0.9)
H(5)	136(5)	150(5)	461(12)	7.9(1.6)

Atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
N(1)	68(2)	75(2)	264(12)	9(4)	−49(9)	−77(10)
C(2)	64(2)	65(2)	273(13)	12(4)	−1(11)	−27(11)
C(3)	66(2)	60(2)	177(11)	12(4)	−1(9)	−21(9)
C(4)	64(2)	59(2)	187(11)	7(4)	15(9)	−23(9)
C(5)	79(3)	72(3)	232(13)	10(5)	−2(11)	32(11)
C(6)	74(3)	87(3)	258(14)	32(5)	−57(11)	−12(12)
C(7)	68(3)	58(2)	197(12)	−14(4)	−33(10)	6(9)
C(8)	67(3)	52(2)	249(13)	2(4)	7(10)	−10(10)
O(1)	74(2)	75(2)	215(9)	13(4)	4(8)	60(8)
O(2)	66(2)	97(2)	326(11)	−22(4)	−46(8)	112(9)
O(3)	81(2)	77(2)	263(10)	−29(4)	82(9)	−47(8)
O(4)	90(2)	109(3)	317(12)	−62(5)	83(10)	−191(11)

continued to reduce the R value to 8.1%. At this stage of refinement, a difference Fourier map was computed, from which the positions of the five hydrogen atoms were located (Fig. 1). There was no significant peak on this map except those due to hydrogen atoms. With anisotropic thermal parameters for non-hydrogen atoms and isotropic thermal parameters for hydrogen atoms, the final R value was 5.90%, excluding un-

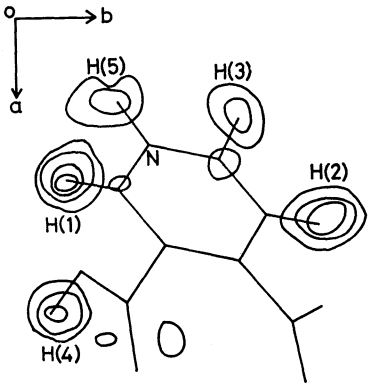


Fig. 1. A composite drawing of the electron density associated with the hydrogen atoms. The contours at intervals of 0.1 e·Å^{-3}, beginning with 0.2 e·Å^{-3} contour.

observed reflections. The $\sum w(F_o-F_c)^2$ function was minimized, where:

$$w = 0.5 \text{ for } |F_o| \leqq 0.5,$$
$$w = 1.0 \text{ for } 0.5 < |F_o| < 6.0 \text{ and}$$
$$w = 6.0/|F_o| \text{ for } 6.0 \leqq |F_o|.$$

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[6] for H atom. The observed and calculated structure factors are listed in Table 2. The fractional coordinates and thermal parameters are listed, along with their estimated standard deviations, in Table 3.

Table 4. Bond lengths (Å) and bond angles (degree)

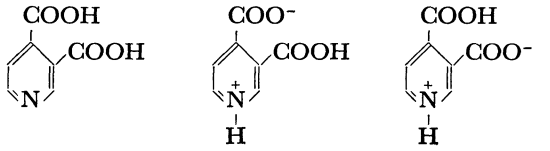
Bond	Length	e.s.d.	Bond	Angle	e.s.d.
N(1)-C(2)	1.336	0.005	C(2)-N(1)-C(6)	122.3	0.3
C(2)-C(3)	1.372	0.005	N(1)-C(2)-C(3)	120.6	0.4
C(3)-C(4)	1.406	0.005	C(2)-C(3)-C(4)	118.6	0.3
C(4)-C(5)	1.377	0.005	C(2)-C(3)-C(7)	120.4	0.3
C(5)-C(6)	1.381	0.006	C(4)-C(3)-C(7)	120.7	0.3
C(6)-N(1)	1.349	0.005	(C3)-C(4)-C(5)	119.4	0.3
C(3)-C(7)	1.502	0.005	C(3)-C(4)-C(8)	121.9	0.3
C(4)-C(8)	1.516	0.005	C(5)-C(4)-C(8)	118.7	0.3
C(7)-O(1)	1.310	0.004	C(4)-C(5)-C(6)	120.0	0.4
C(7)-O(2)	1.201	0.005	C(5)-C(6)-N(1)	119.4	0.4
C(8)-O(3)	1.245	0.004	C(3)-C(7)-O(1)	113.4	0.3
C(8)-O(4)	1.241	0.005	C(3)-C(7)-O(2)	121.2	0.3
C(2)-H(1)	0.98	0.04	O(1)-C(7)-O(2)	125.4	0.3
C(5)-H(2)	0.99	0.05	C(4)-C(8)-O(3)	118.9	0.3
C(6)-H(3)	1.05	0.05	C(4)-C(8)-O(4)	114.2	0.3
O(1)-H(4)	0.94	0.05	O(3)-C(8)-O(4)	126.9	0.4
N(1)-H(5)	1.09	0.06	H(1)-C(2)-N(1)	119	3
			H(1)-C(2)-C(3)	120	3
			H(2)-C(5)-C(4)	120	3
			H(2)-C(5)-C(6)	120	3
			H(3)-C(6)-C(5)	125	3
			H(3)-C(6)-N(1)	116	3
			H(4)-O(1)-C(7)	100	3
			H(5)-N(1)-C(2)	131	3
			H(5)-N(1)-C(6)	105	3

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

Results and Discussion

Molecular Structure. The bond lengths and angles are listed, along with their estimated standard deviations, in Table 4; they are shown in Fig. 2. Figure 3 shows the anisotropic thermal ellipsoids of the non-hydrogen atoms and the isotropic thermal ellipsoids of the hydrogen atoms. The ellipsoids are scaled to include a 74% probability.

The cinchomeronic acid molecule can take the three forms shown below and two intermediate forms between the neutral molecule (A) and the zwitter ions ((B) or (C)).



(A) Neutral molecule (B) Zwitter ion (C) Zwitter ion

The present study has revealed that the molecule takes the form of the zwitter ion (B) in the crystal. This is

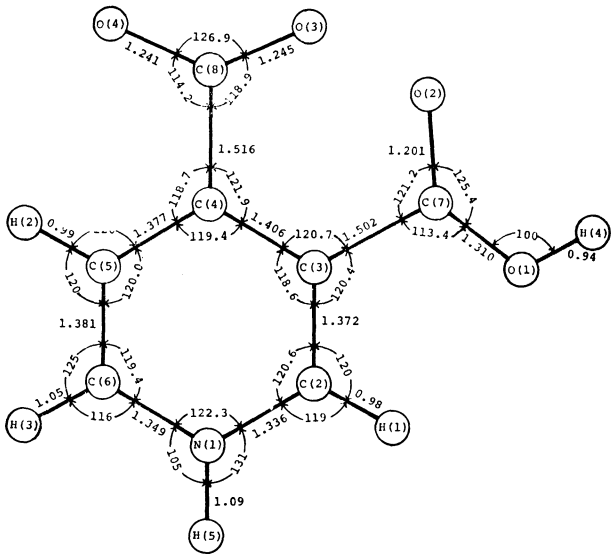


Fig. 2. Dimensions of cinchomeronic acid molecule.

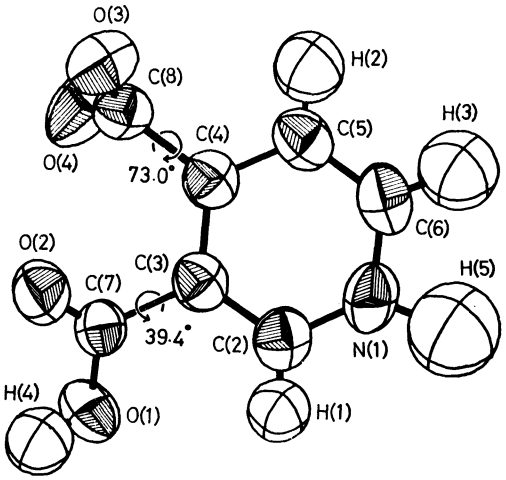


Fig. 3. The anisotropic thermal ellipsoids of non-hydrogen atoms and the isotropic thermal ellipsoids of hydrogen atoms. Ellipsoids are scaled to include a 74% probability.

evident from the position of the hydrogen atom in the difference Fourier map. It is also confirmed by the C(2)–N(1)–C(6) bond angle, 122.3(3)°, and the C(8)–O(3) and C(8)–O(4) bond lengths, 1.245(4) and 1.241(5) Å respectively (the values in parentheses denote the e.s.d.'s in the last digits).

The pyridine ring is essentially planar. The equation of the least-squares plane through six non-hydrogen atoms of the pyridine ring is:

$$0.6248X - 0.3913Y - 0.6756Z = -1.5159,$$

where X, Y, and Z are coordinates in Å along the a, b, and c axes respectively. The maximum deviation of the ring atom from this plane is 0.013 Å. 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 the pyridine ring

Atom	Deviation(Å)	Atom	Deviation(Å)
N(1)	0.002	O(1)	−0.450
C(2)	−0.013	O(2)	0.946
C(3)	0.012	O(3)	0.965
C(4)	0.001	O(4)	−1.153
C(5)	−0.013	H(1)	0.01
C(6)	0.013	H(2)	−0.02
C(7)	0.215	H(3)	−0.02
C(8)	−0.047	H(4)	0.05
		H(5)	0.16

The differences in the corresponding bond lengths and angles of a pyridine ring, the N(1)–C(2) and N(1)–C(6), the C(2)–C(3) and C(6)–C(5), the C(3)–C(4) and C(5)–C(4) bond lengths, the N(1)–C(2)–C(3) and N(1)–C(6)–C(5), and the C(2)–C(3)–C(4) and C(6)–C(5)–C(4) bond angles, are −0.013(5), −0.009(5), 0.019(5) Å, 1.2(4)° and −1.4(3)°. These values show that the pyridine ring has, approximately, the C_{2v} symmetry in the molecule. The slight deviations from C_{2v} symmetry may be due to the substitution of a carboxyl group in the β-position.

In the carboxyl group (C(7)O(1)O(2)H(4)), each C–O bond length is clearly different from the others. Hence, this group consists of C=O and C–O(H) groups. On the other hand, the C(8)–O(3) and C(8)–O(4) bond lengths in another carboxyl group, 1.245(4) and 1.241(5) Å, are equal within the limits of experimental error. This fact suggests that the hydrogen atom moves from the oxygen atom O(4) to the nitrogen atom N(1) of a pyridine ring. The C(7)–O(2) bond length is the shortest of the four C–O bond lengths. This can be explained by the fact that only the O(2) atom does not participate in a hydrogen bond. Similar situations have been observed in dinicotinic acid and quinolinic acid. The difference between the C(3)–C(7) and C(4)–C(8) bond lengths, 0.014(5) Å, lies on the borderline of significance in relation to their estimated standard deviations. A similar tendency has been observed in quinolinic acid. These differences may be caused by the formation of a zwitter ion.

There is no intramolecular hydrogen bond between the adjacent carboxyl groups. The carboxyl groups twist by 39.6° (C(7)O(1)O(2)) and 73.0° (C(8)O(3)-O(4)) out of the plane of the pyridine ring, as is shown in Fig. 3, so that the repulsion between the oxygen atoms is reduced by the twists of the C–C bonds.

Molecular Arrangement and Hydrogen-bond System. The crystal structure is shown in Figs. 4 and 5. The distances and angles of hydrogen bonds are listed in Table 6. The hydrogen bonding system is shown in Fig. 6. In Figs. 4, 5, and 6, the same numbers designate the same molecules. The symmetry codes corresponding to these molecules are shown in Table 6.

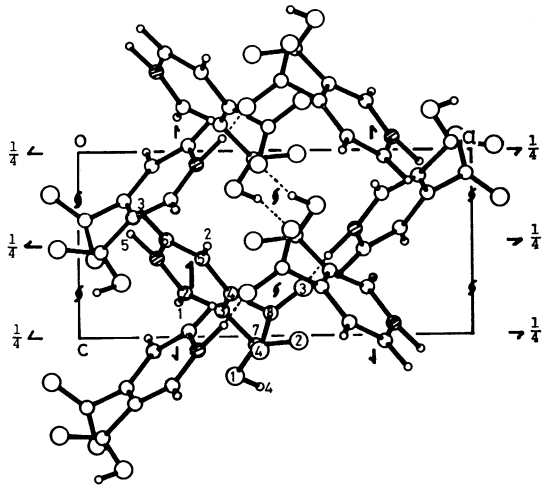


Fig. 4. A view of the crystal structure down the b axis. The hydrogen bonds are shown by broken lines.

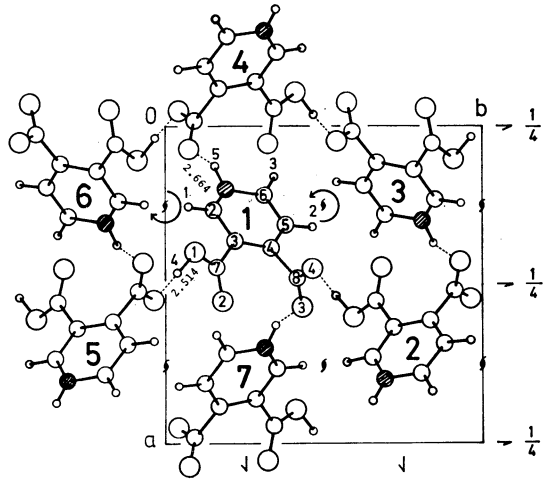


Fig. 5. A view of the crystal structure down the c axis. The hydrogen bonds are shown by broken lines. The ↻ signs around two-fold screw axes indicate the directions of spirals.

The hydrogen bonds are found in two spiral forms around the two-fold screw axes parallel to the c axis, thus linking the molecules three-dimensionally. There are four molecules per turn of spiral along the c axis. The carbonyl oxygen atom O(2) is free from the hydrogen bond, while the nitrogen atom N(1) in a pyridine ring participates in it. This is a remarkable feature of the crystal structures of carboxylic acids with a pyridine ring. This situation has been found in all crystal structures of pyridinecarboxylic acids deter-

Table 6. Hydrogen bond distances (Å) and angles (degree)

X——H·····O	Symmetry	X···O	e.s.d.	X—H	e.s.d.	H···O	e.s.d.	Angle	e.s.d.
O(1)-H(4)···O(4)	(1, 1, 5)	2.514	0.004	0.94	0.05	1.60	0.05	162	5
N(1)-H(5)···O(3)	(1, 1, 4)	2.664	0.004	1.09	0.06	1.59	0.06	166	5
C——O·····Y	Symmetry	Angle	e.s.d.						
C(8)-O(4)···H(4)	(5, 5, 1)	132	2						
C(8)-O(4)···O(1)	(5, 5, 1)	131.0	0.1						
C(8)-O(3)···H(5)	(4, 4, 1)	130	2						
C(8)-O(3)···N(1)	(4, 4, 1)	134.6	0.2						

Symmetry code

1=(x, y, z)	5=(1−x, −1/2+y, 5/2−z)
2=(1−x, 1/2+y, 5/2−z)	6=(1/2−x, −y, 3/2+z)
3=(1/2−x, 1−y, 3/2+z)	7=(1/2+x, 1/2−y, 1−z)
4=(−1/2+x, 1/2−y, 4−z)	8=(x, y, 3+z)

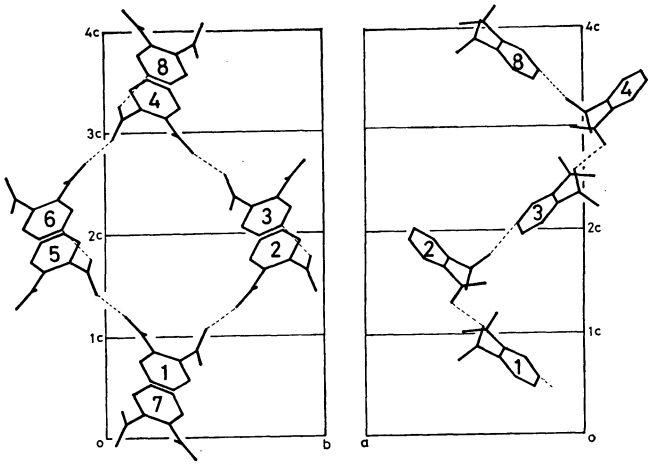


Fig. 6. The hydrogen bonding system.
(a): A view of the spiral down the a axis.
(b): A view of the spiral down the b axis.

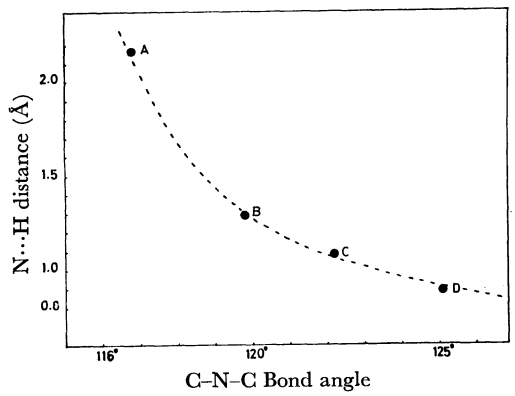


Fig. 7. The relation between the C–N–C bond angle of pyridine ring and the N···H distance for hydrogen bond.
A: Dipicolinic acid (Ref. 2); B: Dinicotinic acid (Ref. 4); C: Cinchomeronic acid (This study); D: Quinolinic acid (Ref. 3).

mined by the X-ray method except for that of one hydrate.

Figure 7 shows the relation between the C–N–C bond angle of a pyridine ring and the N···H distance for a hydrogen bond about four pyridine-dicarboxylic acids. There is a clear correlation between them. This result is an example of the change in electronic

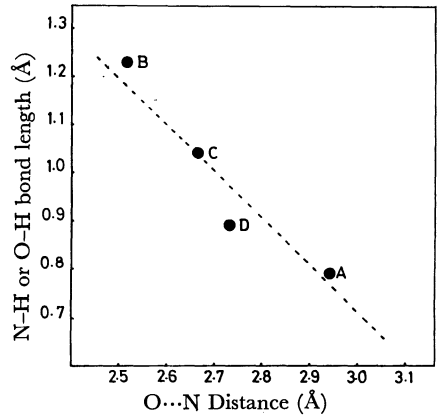


Fig. 8. The variation of the bond length in proton donor group with the O···N distance for hydrogen bond. A, B, C, and D are the same compounds as listed in Fig. 7.

structure in a nitrogen atom corresponding to the variation in interaction between the nitrogen and hydrogen atoms in the hydrogen bond. When the N···H distance is long, as in dipicolinic acid, the nitrogen atom acts as a proton acceptor and gives a C–N–C bond angle similar to that of pyridine[7] itself. On the other hand, the protonated nitrogen atom can be regarded as a proton donor in the case of a short N–H distance, as in quinolinic acid and cinchomeronic acid; it gives a larger C–N–C bond angle than that of pyridine itself in relation to the change in the electronic structure in a nitrogen atom. The situation lies between these two cases in dinicotinic acid. Figure 8 gives the variation in the bond length in a proton donor group with the O···N distance for a hydrogen bond. It may be seen that the stronger interaction occurs between the hydrogen and proton acceptor atoms in the case of the shorter hydrogen bond. Hence, the hydrogen bonds between the nitrogen and oxygen atoms in pyridine-dicarboxylic acids may be classified in terms of the O···N distance in to the following three forms:

(1) O–H···N: long hydrogen bond (longer than 2.75 Å)
(2) $\bar{O}$···H–$\overset{+}{N}$: middle hydrogen bond (2.60—2.75 Å)

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

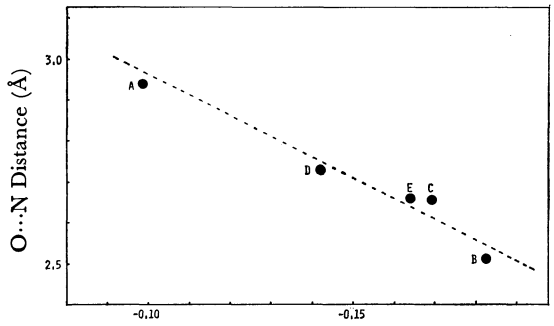


Fig. 9. The relation between the net charge on nitrogen atom calculated by the CNDO method and the O···N distance for hydrogen bond. A, B, C, and D are the same compounds listed in Fig. 7.
E: Nicotinic acid (Ref. 1)

(3) O–H–N: short hydrogen bond (shorter than 2.60 Å)

Using the neutral structures of several pyridinecarboxylic acids, the net charges on the nitrogen atoms were calculated by the use of the "complete neglect of differential overlap" (CNDO) method. They are plotted against the O···N distances in Fig. 9. There is a good linear relation between the calculated net charges on the nitrogen atoms and the observed O···N distances for hydrogen bonds. If this relation can be applied to the O···N hydrogen bonds of other pyridinecarboxylic acids, the O···N distances can be easily predicted by the calculation of the net charges on nitrogen atoms. In conclusion, the strength of the hydrogen bond increases with an increase in the net charge on a nitrogen atom. Moreover, the molecular form may depend on the change in the net charge on a nitrogen atom corresponding to the positions of substituted carboxyl groups.

Computer Programs. All the calculations were performed on a FACOM 270-30 computer at the Computer Center of Osaka City University by the use of the following programs—RSLC-3 (cell constant),[8] RSSFR-3 (Fourier synthesis),[9] HBLS-IV (block-diagonal least-squares refinement),[10] DAPH (bond length, bond angle and least-squares plane),[11] SCALE (film factor, Lp and layer scaling,)[12] TE-I (thermal ellipsoid),[13] CNINDO (CNDO and INDO calculations),[14] and PHASE-I, II, III (symbolic addition).[15]

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