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The Crystal Structure of Quinolinic Acid

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The crystal structure of quinolinic acid (2,3-pyridinedicarboxylic acid) has been determined by the method of X-ray diffraction. The crystal is monoclinic, with a space group of $P2_1/c$ and with cell dimensions of $a=7.421$, $b=12.729$, $c=7.850$ Å, and $\beta=116.96°$. The crystal structure was solved by the inspection of a Patterson map. The final R value was 6.78% for 1224 observed reflections. The quinolinic acid molecule takes the form of a zwitter ion in the crystal. The pyridine ring in the molecules shows a significant deformation from the C_{2v} symmetry of idealized geometry. The lengths of the two C–C bonds joining the carboxyl groups to the ring are longer than the normal value. There is an intramolecular hydrogen bond between the adjacent carboxyl groups. The bond lengths in the two C–O groups which participate in this intramolecular hydrogen bond are longer than those of the other two C–O groups. One of the two carbonyl oxygen atoms participates in a hydrogen bond, while the other is free from it. The molecules are arranged in layers closely parallel to the (0 1 0) plane. Each molecule on the same plane is hydrogen-bonded to form an endless chain along the a axis. These chains are packed 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 O–H···N hydrogen bonding studied based on X-ray crystal structure analyses of some carboxylic acids with a pyridine ring. The O–H···N or $^+$N–H···O hydrogen bond has been found in all the crystals of dipicolinic acid,[1] dinicotinic acid,[2] and cinchomeronic acid[3] thus far studied, without exception. It seems 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 melting point of a quinolinic acid crystal is the lowest of those of the six pyridine dicarboxylic acids, and this molecule has adjacent carboxyl groups. These facts suggest that there is some hydrogen bond which acts not between molecules, but within a molecule. Such an intramolecular hydrogen bond is known in 3,4-furandicarboxylic acid,[4] which has an aromatic five-membered ring. On the contrary, while the crystal structures of five carboxylic acids which have adjacent carboxyl groups substituted on a benzene ring(phthalic acid,[5] trimellitic acid,[6] hemimellitic acid,[7] pyromellitic acid,[8] and mellitic acid[9]) have previously been determined by the X-ray method, no intramolecular hydrogen bond between the adjacent carboxyl groups has been found in their crystal structures. If the geometrical configuration plays an important role in the formation of an intramolecular hydrogen bond between the adjacent carboxyl groups substituted on the aromatic six-membered ring, it may be impossible to form this type of hydrogen bond in crystal. In this regard, it will also be of interest to find out the mode of the hydrogen bond in this crystal.

Experimental

The crystals were obtained in the form of light yellow prisms by recrystallization from an aqueous solution. Weissenberg

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[1] F. Takusagawa, K. Hirotsu, and A. Shimada, This Bulletin, **46**, 2020 (1973).

[2] F. Takusagawa, K. Hirotsu, and A. Shimada, This Bulletin, **46**, 2292 (1973).

[3] F. Takusagawa, K. Hirotsu, and A. Shimada, *Acta Crystallogr.*, **A28**, S15 (1972).

[4] D. E. Williams and R. E. Rundle, *J. Amer. Chem. Soc.*, **86**, 1660 (1964).

[5] H. Jaggi, *Z. Kristallogr.*, **109**, 3 (1957).

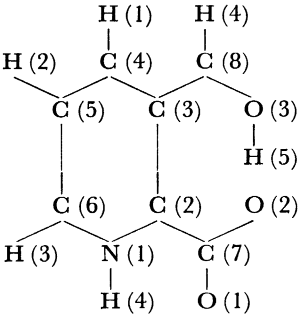
[6] F. Takusagawa, K. Hirotsu, and A. Shimada, This Bulletin, to be published.

[7] F. Takusagawa, K. Hirotsu, and A. Shimada, This Bulletin, to be published.

[8] F. Takusagawa, K. Hirotsu, and A. Shimada, This Bulletin, **44**, 1274 (1971).

[9] S. F. Darlow, *Acta Crystallogr.*, **14**, 159 (1961).

Table 1. Crystal data for quinolinic acid

Molecular formula	$C_7H_5NO_4$
Molecular weight	167.12
Crystal size	~0.3×0.3×0.3 mm
Crystal system	Monoclinic
Space group	$P2_1/c$
Cell dimensions;	
a	7.421±0.006 Å
b	12.729±0.008
c	7.850±0.008
β	116.96±0.08°
V	660.9±0.8 $Å^3$
Z	4
Density (calculated)	1.680 g/cm^3
Density (observed)	1.66
Radiation	Cu $K\alpha(\lambda=1.5418$ Å)
Linear absorption coefficient	14.17 cm^{-1}
Number of independent reflections	1371
The atom numbering 	

photographs showed the crystal to be monoclinic, with a space group of $P2_1/c$. The cell dimensions were measured from zero-layer Weissenberg photographs, which had been calibrated with superimposed Al powder lines. They are given, along with other crystal data, in Table 1. There are four molecules in a unit cell, corresponding to the density of 1.66 g/cm^3 observed by the flotation method. One of the crystals was in the shape of a sphere with the average diameter of 0.3 mm. The intensity data were collected for the 0—10 layers around the b axis and the 0—2 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 were estimated visually by comparison with intensity standard. Of the possible 1513 reflections within a Cu $K\alpha$ sphere, 1371 independent reflections were measured; 147 were too weak to be observed. The absorption coefficient is 14.17 cm^{-1} for Cu $K\alpha$ radiation, and no absorption correction was applied. Appreciable thermal diffuse scattering was observed along the directions of the b* and c* axes on Weissenberg photographs.

Structure Determination and Refinement

The crystal structure was solved by the inspection of a sharpened Patterson map which had been resolved enough to give the orientation and location of the molecules in the unit cell. The first postulated structure gave an R value of 41%, which decreased to 15% after three cycles of least-squares refinement with individual isotropic thermal factors. Since the 0 4 0 reflection seemed to have a strong extinction effect, this reflection was removed from the later refinements.

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

$$w = 0.5 \text{ for } 0.5 \geqq |F_o|,$$

$$w = 1.0 \text{ for } 6.0 > |F_o| > 0.5 \text{ and}$$

$$w = 6.0/|F_o| \text{ for } |F_o| \geqq 6.0.$$

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[10] for the H atom. At the stage of R=9.6%, a difference Fourier map was computed, and from it the positions of the five hydrogen atoms were located (Fig. 1). With anisotropic thermal parameters for non-hydrogen atoms and isotropic thermal parameters for hydrogen atoms, the final R value was 6.78%, 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.

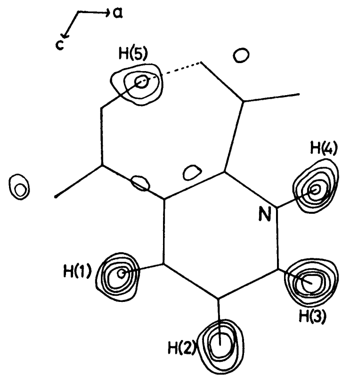


Fig. 1. A composite drawing of the electron density associated with the hydrogen atoms. The contours are at intervals of 0.1 e·$Å^{-3}$, beginning with the 0.2 e·$Å^{-3}$ contour.

Results and Discussion

Molecular Structure. The bond lengths and angles are listed, along with their estimated standard deviations, in Table 4, and they are shown in Fig. 2. Figure 1 shows a difference Fourier map along the b axis, in which there is no high peak except those due to hydrogen atoms. Figure 3 shows the anisotropic thermal ellipsoids of the non-hydrogen atoms and the isotropic thermal ellipsoids of the hydrogen atoms. The net charges and π-bond orders calculated by the CNDO/2 method[11] are shown in Fig. 4.

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

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

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, for which the $|F_o-F_c|/|F_o|$ is larger than 0.3, is indicated by a plus sign.

L	FO	FC	DF
H,K=	0	0	
2	411	-388	-23
4	32	38	-6
6	25	-22	-3
8	41	39	1
H,K=	1	0	
-8	19	-20	0
-6	141	-148	6
-4	60	67	-7
-2	21	-21	0
0	135	-138	2
2	93	-91	-1
4	65	-61	-4
6	126	-125	0
8	67	65	2
H,K=	2	0	
-8	25	23	1
-6+	14	-8	-5
-4	231	-237	6
-2	116	105	11
0	255	-265	9
2	111	131	-19
4	247	-265	18
6	61	51	10
H,K=	3	0	
-8	36	28	8
-6	58	-60	1
-4	170	-146	-23
-2	83	-85	2
0	419	445	-25
2	189	185	3
4	102	93	8
6+	9	5	3
H,K=	4	0	
-10	52	42	10
-8	176	-165	-11
-6	222	223	0
-4	103	91	11
-2	85	-90	4
0	170	169	1
2	144	-150	5
4	37	-36	0
6	71	68	3
H,K=	5	0	
-10	68	-62	-5
-8	98	88	9
-6	72	-75	3
-4	289	326	-36
-2	31	25	5
0	244	-253	9
2	116	122	-6
4	18	21	-3
H,K=	6	0	
-8	125	122	3
-6	47	-46	0
-4	13	11	1
-2	426	-415	-11
0	20	20	0
2	30	-34	3
4	58	47	10
H,K=	7	0	
-8	88	-93	4
-6	31	27	4
-4	168	164	3
-2	49	-49	0
0	33	34	-1
2	61	-47	-14
H,K=	8	0	
-8*	0	0	0
-6	148	137	10
-4	93	85	7
-2	49	44	4
0	35	-27	-7
H,K=	9	0	
-6	41	-37	-3
-4	16	13	2
-2	86	-71	-15
H,K=	0	1	
1	518	496	22
2	113	-122	8
3	254	250	4
4	226	-266	40
5	58	-59	0
6	149	154	-5
7	13	11	1
8	33	-27	-6
H,K=	1	1	
-9	8	-8	0
-8	53	54	-1
-7*	0	9	-9
-6	67	-69	1
-5	77	80	-2
-4	226	222	4
-3	217	-229	11
-2	378	-366	-12
-1	149	-154	4
0	240	241	-1
1	168	-180	12
2	105	85	19
3*	0	5	-5
4	58	65	-6
5	106	-102	-4
6	88	-87	-1
7	83	70	13
8	52	44	8
H,K=	2	1	
-9	14	12	2
-8	103	95	7
-7	19	21	-2
-6	30	31	-1
-5	35	-34	0
-4	245	-263	18
-3	107	-103	-4
-2	316	360	-43
-1	184	-181	-3
0	288	283	5
1	364	-380	16
2	121	-108	-12
3	272	272	0
4	112	108	4
5	116	-116	0
6	32	-23	-9
7	49	-42	-6
H,K=	3	1	
-9+	15	8	7
-8	50	-49	-1
-7	174	165	8
-6	282	-286	4
-5	81	-80	0
-4	12	-11	0
-3	492	-479	-12
-2	106	-101	-5
-1	231	234	-2
0	156	157	0
1	299	304	-4
2	79	76	3
3	118	122	-4
4	352	-347	-5
5*	0	1	-1
6*	0	7	-7
7	29	-33	3
H,K=	4	1	
-10	39	44	-5
-9	16	-11	-4
-8	105	98	6
-7	82	85	-3
-6	59	-61	1
-5	62	-55	-7
-4	20	20	0
-3	166	168	-2
-2	138	139	0
-1	172	-170	-2
0	41	-49	8
1	72	62	10
2	48	45	2
3	25	20	4
4+	28	-20	-8
5	31	-29	-2
6	19	22	-3
H,K=	5	1	
-10	65	56	9
-9	38	-30	-7
-8	18	-13	-4
-7	128	133	-5
-6	136	138	-1
-5	36	-32	-4
-4	114	-120	6
-3	58	58	0
-2	180	181	-1
-1	86	-90	3
0+	0	3	-2
1	66	75	-9
2	98	95	2
3+	19	10	8
4*	0	1	-1
5+	30	-17	-12
H,K=	6	1	
-9*	0	9	-9
-8	44	37	6
-7	36	35	0
-6	121	-131	10
-5	63	-68	4
-4	191	-196	5
-3	179	-188	8
-2	49	42	7
-1	34	-32	-1
0	38	30	7
1	78	-82	4
2	18	-14	-3
3	95	83	11
4	45	-55	9
H,K=	7	1	
-9	43	-40	-3
-8	32	33	-1
-7	37	-31	-5
-6	49	-54	4
-5	67	63	4
-4	214	220	-5
-3	48	-44	-3
-2	120	-116	-3
-1	143	137	5
0	18	-20	1
1	50	-46	-4
2	21	25	-3
H,K=	8	1	
-8	33	29	4
-7	26	-22	-3
-6	35	29	6
-5	82	69	12
-4	30	-25	-5
-3	116	105	11
-2	41	32	8
-1	9	9	0
0	41	-44	2
H,K=	9	1	
-7*	0	2	-2
-6	74	72	1
-5	20	18	1
-4	78	-69	-8
-3	53	-45	-8
-2+	8	2	6
H,K=	0	2	
0	17	-22	4
1	10	12	-1
2	9	-7	-1
3	573	-632	58
4	27	27	0
5	14	-14	0
6	42	-46	4
7	142	142	0
8	12	15	-2
H,K=	1	2	
-9+	8	4	4
-8*	0	1	-1
-7	75	74	0
-6	23	21	1
-5	168	-174	6
-4+	39	-33	-5
-3	324	314	9
-2	46	45	0
-1	351	345	5
0	110	106	4
1	582	-574	-7
2	95	-95	0
3	129	119	9
4	33	31	1
5	107	107	0
6+	11	-2	-9
7+	12	-6	-6
8+	9	0	-8
H,K=	2	2	
-9	22	-19	-3
-8	15	-11	-3
-7	11	-10	0
-6	10	9	1
-5	203	221	-18
-4+	3	4	-1
-3	279	-248	-30
-2	55	-48	-6
-1	385	450	-64
0+	1	0	-1
1	70	-75	5
2	27	29	-1
3	77	92	-15
4	22	-19	-2
5	21	14	6
6	20	15	4
7	56	48	7
H,K=	3	2	
-9	35	-28	-6
-8+	10	-5	-5
-7	244	-262	17
-6+	0	-4	3
-5	84	-88	3
-4+	13	-8	-4
-3	335	-320	-15
-2*	0	3	-3
-1	488	480	7
0	36	-36	0
1	244	-259	15
2	42	45	-3
3	228	-238	10
4	25	-29	4
5	48	-39	-8
6+	13	5	7
7	61	-48	-12
H,K=	4	2	
-9	52	52	0
-8+	3	4	-1
-7*	0	0	0
-6*	0	0	0
-5	256	270	-14
-4	17	-16	0
-3	100	-89	-11
-2	76	80	-3
-1	147	-159	11
0	28	-32	3
1	15	12	3
2*	0	0	0
3	134	137	-3
4	20	19	1
5	18	-22	4
6	11	-9	-2
H,K=	5	2	
-9	16	17	0
-8*	0	-5	5
-7	233	255	-21
-6	20	20	0
-5	100	-100	0
-4	4	-5	0
-3+	15	-7	-8
-2	41	-43	2
-1	128	131	-3
0	36	31	4
1	23	22	1
2	30	-29	-1
3	86	89	-2
4*	0	4	-4
5	62	61	1
H,K=	6	2	
-9*	0	-1	1
-8	12	13	0
-7	37	-38	0
-6	26	-25	0
-5	128	-129	0
-4	47	46	0
-3	249	-261	12
-2	43	-39	-3
-1	55	-55	0
0*	0	6	-6
1	156	180	-23
2*	0	10	-10
3	92	-84	-8
H,K=	7	2	
-9	25	28	-3
-8+	11	6	4
-7	42	40	2
-6*	0	-7	7
-5	95	96	0
-4+	0	1	0
-3	86	-76	-10
-2+	17	10	7
-1+	22	1	21
0*	0	-4	4
1+	13	-8	-5
H,K=	6	2	
-8*	0	-8	8
-7+	21	27	-6
-6	19	15	4
-5	29	31	-2
-4	19	-15	-4
-3	74	-73	-1
-2	12	9	2
-1+	17	-8	-9
0	11	-9	-2
1+	17	24	-6
H,K=	9	2	
-7	35	32	2
-6	16	13	3
-5	15	-10	-4
-4*	0	1	-1
-3	116	-103	-13
-2	9	-8	0
H,K=	0	3	
1	443	-432	-11
2	166	-163	-3
3	205	-191	-13
4	241	-213	-27
5	15	16	-1
6	127	129	-1
7+	16	-10	-6
8	25	-26	1
H,K=	1	3	
-9	9	11	-2
-8	39	49	-10
-7	10	-9	-1
-6	45	-49	3
-5	43	-48	4
-4	228	221	7
-3	174	170	3
-2	389	-417	27
-1	290	287	2
0	402	393	9
1+	11	3	8
2+	23	-37	14
3	63	59	3
4	82	88	-6
5	86	83	2
6	55	-59	4
7	69	-66	-3
8	31	32	0
H,K=	2	3	
-9*	0	-10	10
-8	91	92	0
-7	28	-31	3
-6	27	-26	-1
-5	98	100	-2
-4	146	-147	1
-3	49	-48	0
-2	195	179	16
-1	196	191	4
0	210	219	-9
1	343	342	1
2	14	-12	-1
3	243	-246	3
4	49	47	2
5	114	113	0
6	38	-34	-3
7	53	50	3
H,K=	3	3	
-9*	0	6	-6
-8	16	-13	-2
-7	158	-163	4
-6	282	-283	1
-5	46	42	3
-4	73	-64	-9
-3	437	462	-25
-2	69	72	-3
-1	299	-286	-12
0	95	85	10
1	244	-235	-9
2	62	60	1
3	93	-91	-1
4	282	-297	15
5	24	-25	0
6*	0	-5	5
7+	19	29	-10
H,K=	4	3	
-9	5	-6	0
-8	63	60	2
-7	31	-36	4
-6+	18	-11	-6
-5+	9	-2	-6
-4	25	-24	-1
-3	109	-98	-11
-2	115	113	2
-1	173	171	1
0+	16	-8	-8
1	54	-46	-7
2	24	20	3
3	21	-22	0
4	25	-24	0
5	31	35	-4
6	34	33	1
H,K=	5	3	
-9	9	11	-1
-8	27	-23	-3
-7	104	-103	-1
-6	138	133	4
-5	21	21	0
-4	111	-111	0
-3	59	-56	-3
-2	150	141	8
-1	62	55	6
0	5	4	1
1	67	-70	2
2	93	103	-9
3	26	-20	-5
4+	26	-16	-9
5	32	25	7
H,K=	6	3	
-9*	0	2	-2
-8	54	52	1
-7	36	-40	4
-6	144	-153	9
-5	81	84	-3
-4	153	-155	2
-3	158	154	4
-2	62	60	1
-1	21	24	-3
0+	9	3	5
1	88	96	-7
2+	10	15	-5
3	87	-81	-5
H,K=	7	3	
-9	55	54	1
-8	40	44	-4
-7	13	10	3
-6	50	-56	6
-5	62	-61	0
-4	186	183	2
-3	50	51	0
-2	108	-98	-10
-1	115	-112	-2
0	14	-16	1
1	26	26	0
2+	7	-2	-4
H,K=	8	3	
-8	18	19	0
-7	22	21	0
-6	43	44	-1
-5	47	-54	6
-4	9	-8	-1
-3	127	-113	-13
-2*	0	0	0
-1*	0	3	-3
0+	16	-24	7
H,K=	9	3	
-6	59	58	1
-5*	0	-7	7
-4	58	-59	1
-3	50	43	6
H,K=	0	4	
1	119	-119	0
2	197	215	-18
3	55	-65	10
4	27	-31	4
5	61	67	-6
6	30	27	3
7	37	-39	1
8	38	-40	1
H,K=	1	4	
-9	12	-12	0
-8+	27	18	9
-7*	0	-10	10
-6	95	97	-2
-5	61	67	-6
-4+	6	4	2
-3	30	-29	-1
-2+	21	-11	-9
-1	49	-47	-2
0	89	86	2
1	126	119	7
2	106	96	10
3	75	-76	0
4	38	32	5
5	37	35	1
6	101	106	-4
7+	9	13	-3
8	52	-50	-1
H,K=	2	4	
-9	20	15	4
-8	16	-13	-2
-7	26	-28	1
-6	22	20	1
-5	14	-12	-2
-4	182	162	19
-3+	7	-10	2
-2	28	-24	-3
-1	22	-27	5
0	145	146	0
1	24	-20	-4
2	76	-79	3
3	27	25	2
4	231	235	-3
5	35	-35	0
6	54	-46	-8
7	10	7	2
H,K=	3	4	
-9+	9	12	-3
-8	35	-34	-1
-7	18	-12	-5
-6	68	74	-5
-5	19	16	2
-4	93	68	25
-3	19	14	5
-2	104	96	7
-1	88	90	-2
0	354	-333	-20
1	71	-73	2
2	155	-157	1
3	54	60	-6
4	78	-75	-2
5	25	-24	-1
6*	0	-4	4
H,K=	4	4	
-9+	19	-12	-6
-8	129	128	0
-7	7	7	0
-6	168	-186	18
-5	21	25	-4
-4	80	-63	-17
-3	79	-80	0
-2	45	46	0
-1	76	82	-6
0	118	-111	-6
1	37	-45	8
2	132	130	2
3	11	-13	2
4	11	12	-1
5	24	26	-1
6	46	-52	5
H,K=	5	4	
-9*	0	1	-1
-8	63	-63	0
-7	7	-7	0
-6	45	40	4
-5+	24	17	7
-4	241	-237	-4
-3+	19	-11	-7
-2	27	-23	-3
-1	72	-79	6
0	178	186	-7
1	57	67	-10
2	88	-95	7
3	20	-18	-2
4	17	-13	-3
H,K=	6	4	
-9*	0	3	-3
-8	90	-95	4
-7	25	29	-3
-6	42	43	-1
-5	55	-58	2
-4	29	-25	-3
-3	65	66	0
-2	329	358	-29
-1	8	-10	2
0+	15	-2	-12
1+	15	8	7
2	19	18	0
3	18	14	3
H,K=	7	4	
-9	17	-15	-2
-8	71	75	-3
-7*	0	7	-7
-6	25	-25	0
-5*	0	-5	5
-4	144	-141	-3
-3	24	-21	-2
-2	33	34	-1
-1	15	13	2
0	18	-18	0
1	17	-15	-2
2	46	38	7
H,K=	8	4	
-8+	14	-6	-7
-7*	0	-2	2
-6	130	-121	-9
-5	32	30	1
-4	76	-66	-10
-3	35	-34	-1
-2	43	-41	-1
-1	15	11	4
0	22	18	4
H,K=	9	4	
-6	33	34	0
-5+	15	8	6
-4	15	-19	4
-3*	0	3	-3
H,K=	0	5	
1	286	-260	-26
2	74	77	-2
3	225	-205	-19
4	182	171	11
5	76	77	-1
6	113	-121	8
7	14	-16	2
8	22	22	0
H,K=	1	5	
-9*	0	7	-7
-8	26	-33	6
-7	27	-28	0
-6	40	41	0
-5	45	-45	0
-4	101	-104	2
-3	177	158	19
-2	131	151	-20
-1	44	-49	5
0	60	-52	-7
1	216	212	4
2	130	-123	-6
3	58	-52	-6
4*	0	-6	6
5	70	64	6
6	59	63	-3
7	42	-36	-5
8	31	-30	0
H,K=	2	5	
-9*	0	0	0
-8	67	-64	-3
-7*	0	-7	7
-6	52	-63	10
-5	34	-31	-3
-4	212	201	11
-3	201	181	19
-2	310	-295	-15
-1	106	101	4
0	123	-135	11
1	159	171	-11
2	75	68	6
3	121	-132	10
4	80	-82	1
5	77	76	0
6*	0	1	-1
7	28	26	2
H,K=	3	5	
-9	33	-28	-4
-8	48	48	0
-7	116	-111	-5
-6	214	222	-7
-5	85	81	3
-4+	14	6	7
-3	276	250	26
-2	135	129	6
-1	58	-51	-6
0	102	-98	-4
1	234	-232	-1
2	47	-47	0
3	133	-136	3
4	278	266	11

TABLE 2. (Continued)

L	FO	FC	DF
9	32	31	0
6*	0	-1	1
H,K=	4	5	
-9	20	18	1
-8	93	-102	9
-7	103	-114	11
-6	72	72	0
-4	40	-38	-1
-3	133	-131	-2
-2	57	-62	5
-1	73	67	5
0+	4	-2	-1
1	23	-18	-5
2	28	-26	-1
3	40	-37	-2
4*	0	2	-2
5	16	18	-2
H,K=	5	5	
-9	35	34	0
-8+	9	4	5
-7	100	-108	7
-6	92	-91	0
-5	19	20	0
-4	50	45	4
-3*	0	-5	5
-2	137	-134	-3
-1	51	55	-3
0	29	-20	-8
1	51	-56	4
2	60	-63	2
3+	0	4	-3
4+	12	-7	-5
H,K=	6	5	
-9	12	-13	0
-8	23	-23	0
-7	15	-14	-1
-6	87	94	-7
-5	27	27	0
-4	156	167	-10
-3	156	160	-4
-2	30	-23	-6
-1	46	46	0
0+	15	-10	-4
1	32	38	-5
2	19	17	1
3	55	-56	1
H,K=	7	5	
-8	15	-17	2
-7	26	27	-1
-6	18	21	-3
-5	32	-29	-3
-4	154	-153	0
-3*	0	-2	2
-2	86	81	5
-1	97	-106	9
0	20	19	0
1	52	53	-1
2	26	-32	5
H,K=	8	5	
-8*	0	-12	12
-7+	9	3	5
-6	19	-19	0
-5	59	-55	-4
-4	30	28	1
-3	66	-64	-1
-2	46	-42	-3
-1	34	-29	-4
0	29	36	-7
H,K=	9	5	
-5	30	-34	3
-4	46	48	-2
H,K=	0	6	
0+	9	14	-4
1	100	88	11
2	18	21	-2
3	349	328	20
4	37	-36	0
5	1	0	0
6	82	81	0
7	93	-96	2
8	25	-26	0
H,K=	1	6	
-8*	0	-2	2
-7	36	-37	0
-6	39	-36	-2
-5	87	73	14
-4	46	43	3
-3	139	-128	-11
-2	61	-60	-1
-1	203	-199	-3
0	151	-146	-5
1	242	246	-4
2	122	128	-6
3	46	-44	-2
4	47	-44	-2
5	80	-75	-4
6*	0	4	-4
7*	0	-5	5
H,K=	2	6	
-9	13	10	3
-8	18	16	2
-7*	0	10	-10
-6*	0	-7	7
-5	144	-140	-4
-4*	0	-4	4
-3	78	73	5
-2	58	58	0
-1	151	-167	15
0	17	16	1
1	26	20	5
2	44	-49	4
3	49	-51	1
4	28	28	0
5	15	-12	-3
6	25	-25	0
7	46	-43	-3
H,K=	3	6	
-9	31	32	-1
-8	9	10	0
-7	175	172	2
-6+	20	6	14
-5	108	107	1
-4	20	20	0
-3	170	157	13
-2*	0	2	-2
-1	254	-250	-3
0	45	41	3
1	173	176	-3
2	57	-60	3
3	152	157	-5
4	54	51	2
5	41	34	7
6	13	-11	-2
H,K=	4	6	
-9	30	-31	1
-8*	0	-5	5
-7	28	-25	-3
-6+	11	-3	-7
-5	176	-171	-4
-4	16	16	0
-3	101	96	4
-2	115	-120	4
-1	48	51	-2
0	38	44	-5
1+	10	-7	-3
2*	0	-5	5
3	84	-90	6
4	36	-35	-1
5*	0	-1	1
H,K=	5	6	
-9	20	-21	1
-8*	0	8	-8
-7	150	-157	7
-6	29	-31	2
-5	20	16	3
-4+	15	8	7
-3*	0	2	-2
-2	70	73	-3
-1	82	-80	-2
0	41	-40	-1
1	41	-41	0
2	48	49	-1
3	53	-59	5
4*	0	-7	7
H,K=	6	6	
-9	17	-15	-2
-8	24	-28	3
-7	36	34	2
-6	44	44	0
-5	100	102	-1
-4	80	-80	0
-3	178	184	-6
-2	64	66	-2
-1	45	42	2
0	13	-12	-1
1	109	-114	4
2	17	-16	0
3	46	48	-1
H,K=	7	6	
-8	11	-9	-1
-7	38	-39	1
-6	12	10	1
-5	70	-67	-2
-4	3	-3	0
-3	86	79	7
-2	18	-14	-3
-1	12	-12	0
0*	0	3	-3
1	12	14	-1
H,K=	8	6	
-7+	16	-22	5
-6	22	-25	2
-5	23	-24	1
-4	30	25	4
-3	54	54	0
-2	16	-15	-1
-1*	0	2	-2
H,K=	0	7	
-5+	0	-2	1
1	195	198	-2
2	112	103	9
3	141	130	10
4	125	116	8
5*	0	-2	2
6	86	-81	-5
7+	10	13	-3
8	20	19	0
H,K=	1	7	
-8	27	-30	3
-7	29	24	5
-6	19	15	3
-5+	12	-4	-7
-4	121	-115	-5
-3	88	-91	3
-2	255	223	32
-1	178	-169	-8
0	254	-270	16
1	29	28	0
2	52	55	-2
3	57	-55	-2
4	64	-64	0
5	31	-29	-1
6	22	19	2
7	32	30	2
H,K=	2	7	
-8	58	-54	-3
-7	24	20	4
-6	35	33	1
-5	74	-74	0
-4	54	50	3
-3	63	54	8
-2	58	-51	-7
-1	111	-114	2
0	60	-68	7
1	135	-137	1
2	53	-54	1
3	97	93	3
4	21	18	3
5	70	-72	1
6	26	24	1
H,K=	3	7	
-8	17	-16	-1
-7	103	103	0
-6	205	209	-3
-4	83	76	6
-3	249	-229	-19
-2	109	-115	5
-1	143	145	-1
0	17	-13	-4
1	123	129	-5
2	34	-31	-3
3	82	76	6
4	174	188	-13
5	14	15	-1
6	16	15	1
H,K=	4	7	
-9	14	13	1
-8	31	-30	-1
-7	21	20	1
-6*	0	0	0
-5	21	17	3
-4	27	21	5
-3	31	24	6
-2	29	-28	-1
-1	81	-86	4
0	55	-48	-6
1*	0	-10	10
2*	0	4	-4
3	31	33	-1
4	14	15	0
5	22	-27	4
H,K=	5	7	
-8	20	17	2
-7	55	53	1
-6	87	-84	-3
-5*	0	1	-1
-4	59	56	3
-3*	0	10	-10
-2	88	-83	-4
-1*	0	7	-7
0	20	-16	-4
1	53	52	1
2	64	-68	3
3	14	11	2
4	20	20	0
H,K=	6	7	
-8	41	-47	5
-7	22	19	2
-6	108	122	-13
-5	58	-56	-1
-4	88	91	-3
-3	93	-96	2
-2	53	-53	0
-1	35	-34	0
0	22	23	0
1	55	-63	7
2	36	-37	1
H,K=	7	7	
-8	33	-36	2
-7	12	10	1
-6	30	35	-5
-5	29	28	0
-4	89	-96	6
-3	16	-13	-2
-2	59	57	1
-1	59	58	0
0	16	16	0
1	18	-18	0
H,K=	8	7	
-6	42	-47	5
-5	33	27	6
-4*	0	-1	1
-3	76	79	-3
-2	13	14	-1
-1+	12	5	6
H,K=	0	8	
0	766	796	-29
1	68	75	-6
2	24	-25	0
3	55	55	0
4+	36	22	13
5	54	-52	-1
6	30	-25	-4
7	32	32	0
H,K=	1	8	
-8	19	-14	-5
-7*	0	11	-11
-6	23	-20	-2
-5	60	-56	-3
-4	89	-79	-9
-3*	0	3	-3
-2	25	21	4
-1	36	31	5
0	25	-26	1
1	72	-72	0
2	90	-78	-12
3	47	44	2
4*	0	0	0
5	34	-31	-2
6	69	-68	-1
7	14	-16	1
H,K=	2	8	
-8*	0	0	0
-7	25	24	0
-6	36	-39	2
-5	25	20	4
-4	75	-61	-13
-3	24	21	2
-2	38	-30	-7
-1*	0	4	-4
0	30	-28	-1
1	32	30	2
2+	15	10	4
3*	0	-11	11
4	156	-165	8
5	31	30	1
6	30	29	1
H,K=	3	8	
-8	38	37	1
-7	11	13	-2
-6	70	-74	3
-5	31	-28	-3
-4	28	21	7
-3	15	-11	-4
-2	99	-96	-2
-1	63	-67	3
0	174	185	-10
1	44	41	2
2	95	95	0
3	53	-48	-4
4	46	43	2
5	22	21	0
H,K=	4	8	
-8	65	-64	0
-7*	0	-1	1
-6	110	117	-7
-5	17	-18	1
-4	43	32	10
-3	58	58	0
-2+	0	-1	0
-1	58	-58	0
0	36	33	3
1	43	41	1
2	83	-84	1
3*	0	7	-7
4	23	18	4
H,K=	5	8	
-8	22	22	0
-7*	0	2	-2
-6*	0	0	0
-5+	14	-9	-5
-4	102	99	3
-3	22	19	3
-2	24	21	3
-1	63	64	-1
0	78	-83	4
1	52	-54	2
2	50	51	0
3	14	14	0
H,K=	6	8	
-8	43	47	-4
-7	33	-31	-1
-6	33	-33	0
-5	47	46	0
-4	38	34	4
-3	58	-53	-4
-2	217	-236	19
-1*	0	0	0
0	22	-22	0
1	15	-14	-1
2+	8	1	6
H,K=	7	8	
-7*	0	0	0
-6	21	21	0
-5*	0	5	-5
-4	89	94	-4
-3	28	24	4
-2	12	-12	0
-1*	0	-5	5
0*	0	-1	1
H,K=	8	8	
-6	73	81	-7
-5	22	-27	4
-4	34	34	0
-3	32	31	0
-2	32	32	0
H,K=	0	9	
0*	0	0	0
1	116	106	9
2	48	-45	-2
3	108	108	0
4	84	-69	-15
5	43	-50	6
6	53	68	-14
7	16	17	0
H,K=	1	9	
-8*	0	12	-12
-7	30	32	-2
-6*	0	-10	10
-5*	0	11	-11
-4	26	23	2
-3	64	-62	-2
-2	73	-57	-15
-1	23	25	-1
0	48	43	5
1	105	-104	0
2	69	67	1
3	59	47	11
4	16	-14	-1
7*	0	8	-8
H,K=	2	9	
-8	33	31	1
-7*	0	2	-2
-6	44	48	-3
-5	24	17	6
-4	76	-74	-2
-3	108	-113	4
-2	156	146	10
-1	57	-54	-3
0	17	21	-3
1	41	-43	2
2*	0	0	0
3	30	30	0
4	33	32	1
5	37	-39	2
6	9	11	-2
H,K=	3	9	
-8	24	-27	2
-7	61	61	0
-6	139	-141	2
-5	56	-52	-3
-4	34	-31	-2
-3	103	-101	-2
-2	55	-57	2
-1*	0	-7	7
0	21	16	5
1	112	118	-5
2	14	11	2
3	97	101	-3
4	139	-146	7
5	31	-33	2
H,K=	4	9	
-8	58	70	-11
-7	88	90	-2
-6	42	-38	-4
-5	41	-33	-8
-4	21	20	1
-3	58	53	5
-2*	0	1	-1
-1*	0	-6	6
0	45	44	1
1*	0	0	0
2*	0	4	-4
3	43	42	1
4*	0	8	-8
H,K=	5	9	
-8*	0	-1	1
-7	48	56	-8
-6	48	45	2
-5+	21	-14	-6
-4	14	12	1
-3	18	-18	0
-2	73	71	1
-1	18	-19	1
0	26	28	-2
1	27	28	0
2	32	35	-2
3*	0	-4	4
H,K=	6	9	
-7*	0	6	-6
-6	63	-66	3
-5	10	-8	-1
-4	101	-103	1
-3	101	-102	0
-2+	15	9	5
-1	37	-36	0
0	13	-16	2
1	12	-16	3
2+	9	-5	-3
H,K=	7	9	
-6+	8	4	3
-5*	0	7	-7
-4	65	66	-1
-3	27	25	2
-2	38	-36	-2
-1	49	57	-8
0	12	-13	1
H,K=	0	10	
0+	15	10	4
1	97	-102	4
2	29	-28	0
3	123	-123	0
4	12	11	0
5	2	2	0
6	49	-52	3
7	46	51	-5
H,K=	1	10	
-7	8	9	-1
-6	28	24	4
-5	16	-12	-4
-4	14	-15	0
-3	34	33	0
-2	36	34	1
-1	109	106	2
0	72	77	-4
1	59	-61	1
2	53	-52	0
3	12	13	-1
4	19	17	1
5	42	38	4
6*	0	-2	2
H,K=	2	10	
-7*	0	-5	5
-6*	0	-6	6
-5	70	68	1
-4*	0	-2	2
-3+	22	15	6
-2	21	-21	0
-1	34	34	0
0	22	-21	0
1	13	-12	-1
2	32	32	0
3	14	13	1
4	13	-13	0
5	11	13	-1
6+	10	14	-4
H,K=	3	10	
-7	81	-90	8
-6*	0	-4	4
-5	89	-85	-3
-4	22	-16	-6
-3	68	-63	-5
-2	16	-13	-2
-1	89	83	5
0+	11	-7	-4
1	92	-91	-1
2	22	15	6
3	87	-85	-1
4	36	-32	-4
5	30	-26	-3
H,K=	4	10	
-7	34	33	0
-6*	0	8	-8
-5	81	77	4
-4*	0	2	-2
-3	78	-72	-6
-2	66	62	3
-1+	12	5	6
0	12	-12	0
1*	0	4	-4
2*	0	9	-9
3	44	50	-5
4	24	24	0
H,K=	5	10	
-7	63	71	-7
-6	16	15	1
-5	33	29	3
-4*	0	-5	5
-3*	0	7	-7
-2	47	-46	-1
-1	46	42	4
0*	0	5	-5
1	42	40	1
2	26	-27	0
H,K=	6	10	
-7	22	-25	2
-6	24	-26	1
-5	64	-62	-2
-4	51	51	0
-3	96	-108	12
-2	40	-39	0
-1	26	-24	-2
0	10	7	2
1	42	53	-10
H,K=	7	10	
-6*	0	0	0
-5	35	37	-2
-4*	0	3	-3
-3	57	-62	4
-2*	0	3	-3
-1*	0	9	-9
H,K=	0	11	
1	86	-88	2
2	34	-31	-2
3	90	-82	-8
4	68	-65	-3
5*	0	0	0
6	44	45	0
H,K=	1	11	
-7	26	-22	-3
-6*	0	-4	4
-5+	26	18	7
-4	48	42	6
-3	54	50	3
-2	84	-74	-10
-1	76	78	-1
0	125	136	-10
1*	0	0	0
2	21	-16	-5
3	22	22	0
4	42	37	4
5*	0	3	-3
H,K=	2	11	
-7*	0	-3	3
-6	14	-10	-4
-5	32	31	1
-4	34	-31	-3
-3	20	-16	-4
-2	28	28	0
-1	44	47	-2
0*	0	2	-2
1	36	38	-2
2	40	38	2
3*	0	-4	4
4	30	-29	0
5	32	35	-3
H,K=	3	11	
-7	45	-49	3
-6	116	-122	6
-5+	12	6	5
-4	51	-48	-3
-3	86	78	8
-2	65	60	5
-1	49	-48	0
0*	0	0	0
1	66	-64	-2
2	19	15	3
3	55	-57	1
4	89	-103	14
H,K=	4	11	
-7	17	-19	1
-6	10	-13	2
-5	12	-10	-1
-4*	0	-1	1
-3*	0	-2	2
-2	16	-12	-4
-1	33	34	0
0	51	50	0
1	26	26	0
2*	0	-2	2
3	26	-27	0
H,K=	5	11	
-7	23	-20	-2
-6	36	40	-4
-5*	0	-6	6
-4	26	-22	-3
-3*	0	6	-6
-2	57	53	4
-1	31	-27	-4
0	17	15	2
1	32	-32	0
2	25	27	-2
H,K=	6	11	
-6	64	-67	3
-5	22	25	-2
-4	43	-47	4
-3	54	55	-1
-2	27	29	-1
-1	34	32	1
0	17	-20	3

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(A^2).

Atom	x	y	z	B(Å^2)
N (1)	9366 (3)	1222 (2)	1061 (3)	—
C (2)	7353 (3)	1248 (2)	−36 (3)	—
C (3)	6118 (3)	1262 (2)	885 (3)	—
C (4)	7064 (3)	1226 (2)	2882 (3)	—
C (5)	9135 (4)	1217 (2)	3937 (3)	—
C (6)	10290 (3)	1221 (2)	2956 (3)	—
C (7)	6823 (4)	1213 (2)	−2183 (4)	—
C (8)	3827 (3)	1329 (2)	−73 (4)	—
O (1)	8242 (3)	1077 (2)	−2534 (3)	—
O (2)	5008 (3)	1351 (2)	−3382 (3)	—
O (3)	2872 (3)	1523 (2)	−1843 (3)	—
O (4)	2985 (3)	1189 (2)	944 (3)	—
H (1)	601 (4)	115 (2)	336 (4)	3.4 (0.6)
H (2)	984 (5)	126 (2)	536 (5)	4.6 (0.8)
H (3)	1155 (5)	119 (2)	331 (5)	4.2 (0.7)
H (4)	1010 (6)	120 (3)	43 (5)	5.0 (0.8)
H (5)	354 (6)	125 (3)	−266 (5)	5.4 (0.9)

Atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
N (1)	131 (4)	59 (2)	143 (4)	3 (4)	175 (7)	8 (4)
C (2)	150 (5)	41 (2)	127 (4)	0 (4)	155 (7)	4 (4)
C (3)	130 (5)	45 (2)	149 (4)	2 (4)	157 (8)	3 (4)
C (4)	140 (5)	56 (2)	143 (4)	3 (4)	176 (8)	2 (4)
C (5)	162 (5)	65 (2)	118 (4)	12 (5)	137 (8)	6 (4)
C (6)	106 (4)	71 (2)	145 (2)	5 (5)	114 (8)	6 (5)
C (7)	178 (6)	63 (2)	149 (5)	−10 (5)	203 (9)	−2 (5)
C (8)	129 (5)	54 (2)	170 (5)	−6 (4)	154 (8)	−12 (5)
O (1)	211 (5)	114 (2)	164 (4)	3 (5)	254 (7)	−10 (5)
O (2)	167 (4)	104 (2)	124 (4)	9 (4)	97 (6)	16 (4)
O (3)	130 (4)	121 (2)	165 (4)	21 (5)	116 (6)	33 (5)
O (4)	140 (4)	100 (2)	225 (5)	−9 (4)	244 (7)	1 (4)

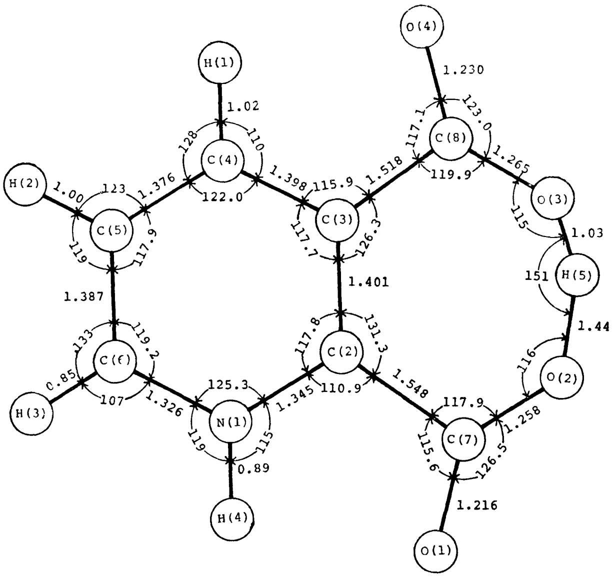


Fig. 2. Dimensions of quinolinic acid molecule.

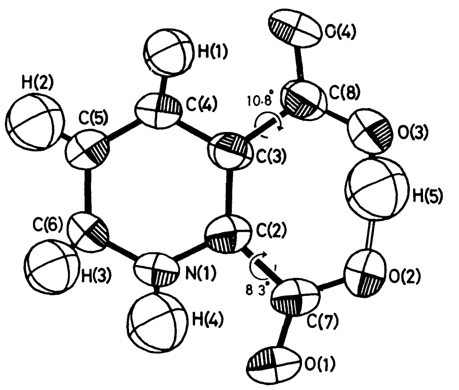


Fig. 3. The anisotropic thermal ellipsoids of non-hydrogen atoms and the isotropic thermal ellipsoids of hydrogen atoms. Ellipsoids are scaled to include 74% probability.

Table 4. Intramolecular bond lengths and angles

Bond	Length	e.s.d.	Bond	Angle	e.s.d.
N (1)-C (2)	1.345 Å	0.003 Å	C (2)-N (1)-C (6)	125.3°	0.2°
C (2)-C (3)	1.401	0.004	N (1)-C (2)-C (3)	117.8	0.2
C (3)-C (4)	1.398	0.004	N (1)-C (2)-C (7)	110.9	0.2
C (4)-C (4)	1.376	0.004	C (3)-C (2)-C (7)	131.3	0.2
C (5)-C (6)	1.387	0.004	C (2)-C (3)-C (4)	117.7	0.2
C (6)-N (1)	1.326	0.003	C (2)-C (3)-C (8)	126.3	0.2
C (2)-C (7)	1.548	0.004	C (4)-C (3)-C (8)	115.9	0.2
C (3)-C (8)	1.518	0.004	C (3)-C (4)-C (5)	122.0	0.2
C (7)-O (1)	1.216	0.004	C (4)-C (5)-C (6)	117.9	0.3
C (7)-O (2)	1.258	0.004	C (5)-C (6)-N (1)	119.2	0.3
C (8)-O (3)	1.265	0.004	C (2)-C (7)-O (1)	115.6	0.3
C (8)-O (4)	1.230	0.004	C (2)-C (7)-O (2)	117.9	0.2
C (4)-H (1)	1.02	0.03	O (1)-C (7)-O (2)	126.5	0.3
C (5)-H (2)	1.00	0.04	C (3)-C (8)-O (3)	119.9	0.3
C (6)-H (3)	0.85	0.04	C (3)-C (8)-O (4)	117.1	0.3
N (1)-H (4)	0.89	0.04	O (3)-C (8)-O (4)	123.0	0.3
O (2)-H (5)	1.44	0.04	H (1)-C (4)-C (3)	110	2
O (3)-H (5)	1.03	0.04	H (1)-C (4)-C (5)	128	2
			H (2)-C (5)-C (4)	123	2
			H (2)-C (5)-C (6)	119	2
			H (3)-C (6)-C (5)	133	3
			H (3)-C (6)-N (1)	107	3
			H (4)-N (1)-C (2)	115	3
			H (4)-N (1)-C (6)	119	3
			H (5)-O (2)-C (7)	116	2
			H (5)-O (3)-C (8)	115	2
			O (2)-H (5)-O (3)	151	4

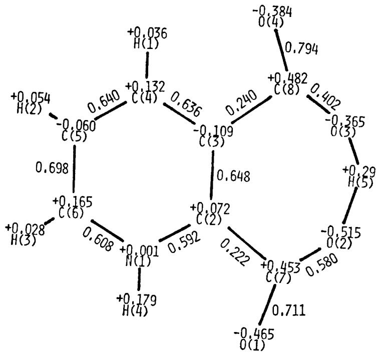
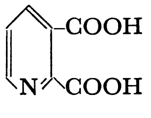
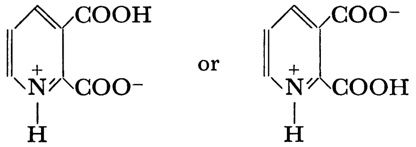


Fig. 4. The net charges and π-bond orders calculated by the CNDO/2 method.

The quinolinic acid molecule may be a mixture of the following two forms:



(A)



(B)

However, the present study shows that the molecule takes the zwitter ion(B) in the crystal. The existence of the molecule in this form is quite evident from the assignment of a hydrogen atom in the difference Fourier map. It is also confirmed by the C(2)–N(1)–C(6) bond angle of 125.3(2)° and by the four C–O bond lengths of 1.216 (4), 1.258(4), 1.265(4), and 1.230(4) Å in the two carboxyl groups (the values in parentheses denote e.s.d.'s in their last digits).

The quinolinic acid molecule is approximately planar, with a maximum deviation of 0.242 Å. The pyridine ring is planar, the maximum deviation of a ring atom from the least-squares plane being 0.013 Å. The equations of the two planes through twelve non-hydrogen atoms of a molecule and six non-hydrogen atoms of a pyridine ring are:

$$0.0551X+0.9983Y+0.0215Z=1.8705 \quad \text{and}$$

$$0.0117X+0.9998Y+0.0156Z=1.6535$$

respectively, 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 respectively. The displacements of all the atoms from these two planes are listed in Table 5.

The pyridine ring in the molecule shows a significant deformation from the C_{2v} symmetry of idealized geometry. The differences between the corresponding bond lengths, the N(1)–C(2) and N(1)–C(6), the C(2)–C(3) and C(5)–C(6), and the C(3)–C(4) and C(4)–C(5) bonds, are 0.019(3), 0.014(4), 0.022(4) Å respectively. The bond lengths of the side which has both carboxyl groups are longer than those of the other side. This difference may depend on the asymmetric substitution of two carboxyl groups, because no such difference has been found in dipicolinic acid[1)] and

Table 5.

(1) The distances from the least-squares plane defined by twelve non-hydrogen atoms of a molecule.

Atom	Deviation(Å)	Atom	Deviation(Å)
N (1)	−0.061	O (1)	0.154
C (2)	−0·016	O (2)	−0.066
C (3)	0.021	O (3)	−0.190
C (4)	0.038	O (4)	0.242
C (5)	−0.031	H (1)	0.17
C (6)	−0.088	H (2)	0.11
C (7)	0.040	H (3)	0.10
C (8)	0.025	H (4)	−0.06
		H (5)	0.12

(2) The distances from the least-squares plane defined by the six non-hydrogen atoms of pyridine ring.

Atom	Deviation(Å)	Atom	Deviation(Å)
N (1)	0.009	O (1)	0.229
C (2)	0.002	O (2)	−0.086
C (3)	−0.012	O (3)	−0.297
C (4)	0.013	O (4)	0.108
C (5)	−0.001	H (1)	0.11
C (6)	−0.010	H (2)	−0.08
C (7)	0.065	H (3)	0.02
C (8)	−0.071	H (4)	0.04
		H (5)	0.05

dinicotinic acid,[2)] in which two carboxyl groups are substituted symmetrically on the pyridine ring.

The lengths of the two C–C bonds joining the carboxyl groups to the ring are 1.548(4) and 1.518(4) Å, longer than the normal value(about 1.48∼1.50 Å for sp^2—sp^2 bond); the difference between these two bond lengths, 0.030(4), is significant, judging from their estimated standard deviations. The two C–O bond lengths in each carboxyl group are slightly different from each other. In carbonyl groups, the difference between the C(7)–O(1) and C(8)–O(4) bond lengths, 0.014(4) Å, is due to the fact that the O(4) atom participates in the hydrogen bond, while the O(1) atom is free from it. Similar differences were also observed in dinicotinic acid[2)] and cinchomeronic acid.[3)] On the other hand, the C(7)–O(2) and C(8)–O(3) bond lengths, 1.258(4) and 1.265(4) Å, are equal within the limits of experimental errors. Their average value, 1.262 Å, is shorter than the normal bond length between the carbon and hydroxyl oxygen atom, and lies between the values of the C=O and C–O(H) bond lengths. The reason for these abnormal C–O(H) bond lengths is the formation of an intramolecular hydrogen bond which joins the O(2) and O(3) atoms at a very short distance, 2.399(3) Å. A similar tendency was observed in carboxyl groups of 3,4-furandicarboxylic acid.[4)] The H(5) atom is bonded to the O(3) atom rather than to the O(2) atom in this analysis, corresponding to the slight difference between C–O distances related to these two oxygen atoms. In connection with this finding, it is desirable to locate the position of this hydrogen atom by neutron-diffraction study, since there has been a speculation that the hydrogen atom might be placed symmetrically between the oxygen atoms when they are joined by a short hydrogen bond. There is a good correlation between the π-bond orders and the observed bond lengths, as is shown in Fig. 4. The C(3)–C(2)–C(7) and C(2)–C(3)–C(8) bond angles deviate greatly from 120° due to the sp^2 hybridization of the C(2) and C(3) atoms. These deviations are caused by the formation of an intramolecular hydrogen bond. Both carboxyl groups are twisted by −8.3° (C(7)O(1)O(2)) and 10.8° (C(8)O(3)O(4)) out of the plane of the pyridine ring, as is shown in Fig. 3, so that the O(2) and O(3) atoms approach each other.

The intramolecular hydrogen bond between the adjacent carboxyl groups was found in 3,4-furandicarboxylic acid,[4)] with an aromatic five-membered ring. However, the intramolecular hydrogen bond of this type has not thus far been found in the crystal structures of carboxylic acids with a benzene ring and another aromatic six-membered ring. From a geometrical point of view, the formation of the hydrogen bond of this type seems to be more difficult in the carboxylic acids with an aromatic six-membered ring than in those with a five-membered ring. Hence it may be noted that the hydrogen bond of this type has been found in the crystal of quinolinic acid, which has an aromatic six-membered ring.

Molecular Arrangement and Hydrogen-bond System. The crystal structure is shown in Figs. 5 and 6. The distances and angles of hydrogen bonds are listed in Table 6. The molecules are arranged in layers closely parallel to the (0 1 0) plane at y=1/8, 3/8, 5/8 and 7/8. These planes have a spacing of 3.182 Å. The dihedral angle which the best plane of a molecule makes with the (0 1 0) plane is 3.3°. Figure 5 is a view parallel to the (0 1 0) plane. Figure 6 is a view normal to the (0 1 0) plane and illustrates the relative orientation of the molecules in two neighboring layers. Figures 6(a) and 6(b) show the relation between the planes

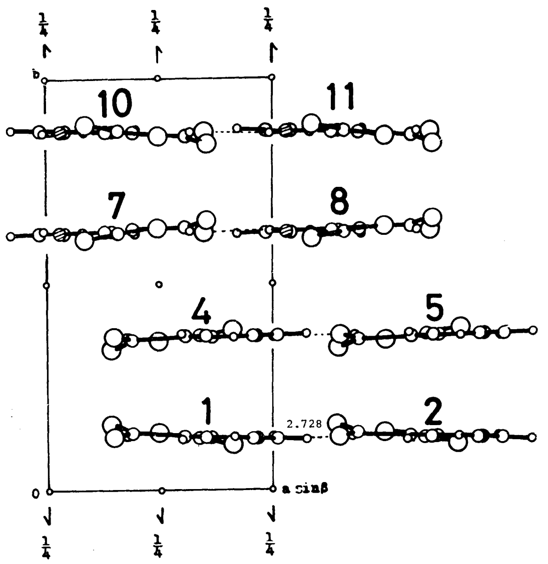


Fig. 5. A view of the crystal structure down the *c* axis. The hydrogen bonds are shown by broken lines.

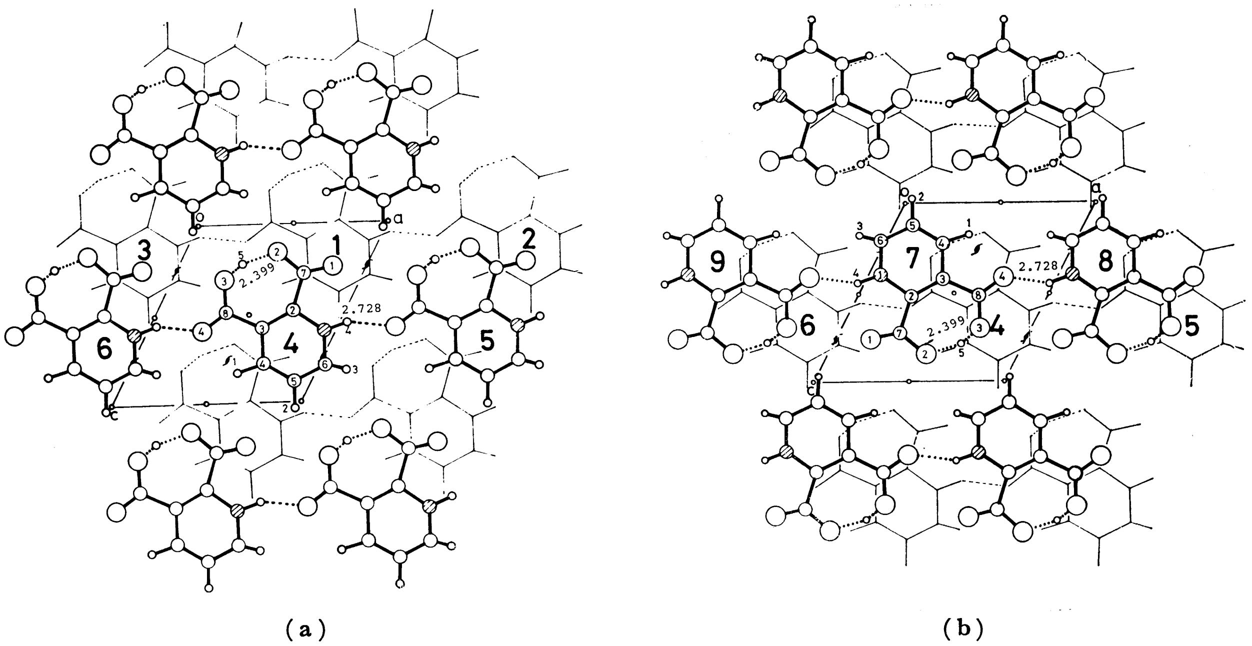


Fig. 6. A view of the crystal structure down the *b* axis, showing the relative orientation of the molecules in two adjacent layers parallel to the (010) plane. (a): The relation between the planes at $y=1/8$ and 3/8 related by the c-glide at $y=1/4$. (b): The relation between the planes at $y=3/8$ and 5/8 related by the center of symmetry at $y=1/2$.

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.
N(1)-H(4)..O(4)	(1, 1, 2)	2.728	0.003	0.89	0.04	1.99	0.04	140	4
O(3)-H(5)..O(2)	(1, 1, 1)	2.399	0.003	1.03	0.04	1.44	0.04	151	4
C——O....X	Symmetry	Angle	e.s.d.						
C(8)-O(4)..H(4)	(2, 2, 1)	133	4						
C(8)-O(4)..N(1)	(2, 2, 1)	144.8	0.2						
C(7)-O(2)..H(5)	(1, 1, 1)	116	2						
C(7)-O(2)..O(3)	(1, 1, 1)	128.7	0.2						

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

at $y=1/8$ and 3/8, and 3/8 and 5/8. In Figs. 5 and 6, the same numerals designate the same molecules. The symmetry codes of the molecules with these numbers are shown in Table 6.

Each molecule on the same plane is joined, through the N(1)-H(4)···O(4) hydrogen bond, with two neighboring molecules and forms an endless chain along the *a* axis. The carbonyl oxygen atom, O(4), participates in a hydrogen bond(O(4)···H(4)-N(1); 2.728(3) Å), while another atom (O(1)) is free from the hydrogen bond. Similar situations are observed also in nicotinic acid,[12] dinicotinic acid,[2] and cinchomeronic acid.[3] Those facts suggest that the O-H···N or $^{+}$N-H···O hydrogen bond is more energetically favored than the O-H···O hydrogen bond in solids.

There is no hydrogen bond between the chains on the same plane, those on the planes at $y=1/8$ and 3/8 related by the c-glide plane at $y=1/4$, and those on the planes at $y=3/8$ and 5/8 related by the center of symmetry at $y=1/2$. These chains are packed together only by the van der Waals forces. Therefore, there is an anisotropy of the bonding forces joining the molecules in this crystal. The appreciable thermal diffuse scattering along the directions of the b^* and c^* axes may be caused by this anisotropy of the bonding forces. Similar patterns were observed in dipicolinic acid monohydrate[1] and other crystals in which molecules are joined by this type of hydrogen bond.[13]

Computer Programs. All the calculations were performed on a FACOM 270–30 computer at the Computer Center of Osaka City University by the use

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[12] W. B. Wright and G. S. D. King, *Acta Crystallogr.*, **6**, 305 (1953).

[13] J. L. Amorós and M. Amorós, "Molecular Crystals," John Wiley and Sons, Inc., New York (1968).

of the following programs—RSLG-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] CNINDO(CNDO and INDO calculation),[11] and TE-I(thermal ellipsoid).[19]

This paper is dedicated to the late Dr. Walter C. Hamilton, who took an interest in the intramolecular hydrogen bond of this compound. The authors wish to express their thanks to Dr. Kichisuke Nishimoto of this faculty for his useful advice in the CNDO calculation.

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14) T. Sakurai, "The Universal Crystallographic Computing System (I)," edited by T. Sakurai, The Crystallographic Society of Japan (1967) p. 18.

15) T. Sakurai, *ibid.*, p. 45.

16) T. Ashida, *ibid.*, p. 65.

17) T. Ashida, *ibid.*, p. 76.

18) H. Yoshioka, K. Hirotsu, and F. Takusagawa, Unpublished work.

19) F. Takusagawa, Unpublished work.