Acta Cryst. (1976). B**32**, 511

Topochemical Studies. VI.* The Crystal and Molecular Structure of 2,5-Pyridinedicarboxylic Acid–*N*,*N*-Dimethylformamide Monohydrate

BY KUNIAKI ITO, SETSUO KASHINO AND MASAO HAISA

Department of Chemistry, Faculty of Science, Okayama University, Tsushima, Okayama 700, *Japan*

(*Received* 6 *May* 1975; *accepted* 26 *June* 1975)

2,5-Pyridinedicarboxylic acid (ICA) crystallizes as a monohydrated complex with *N*,*N*-dimethylformamide (DMF). The structure of the complex has been determined from visually estimated Cu $K\alpha$ data. The crystals are monoclinic, $P2_1/a$, $Z=4$, with $a=14{\cdot}14$ (1), $b=7{\cdot}225$ (4), $c=12{\cdot}28$ (1) Å, $\beta=97{\cdot}3$ (1)°. The structure, containing a disordered DMF molecule, was solved by the Patterson method, and refined by the block-diagonal least-squares method to a final R value of 0·082 for 1683 non-zero reflexions. Molecular layers are stacked on the (401) planes, with a spacing of 3·45 Å between the pyridine rings. In each layer, the carboxyl groups of an ICA molecule are hydrogen bonded with the carbonyl group of the DMF at the 5-position and with an adjacent ICA at the 2-position through two water molecules to form a dimeric unit. The units are linked by the hydrogen bond between the N atom of the pyridine ring and the hydroxyl group of the water to form a ribbon along **b**.

Introduction

Takusagawa, Hirotsu & Shimada (1973*a–d*) have systematically studied the crystal structures of pyridinedicarboxylic acids, *i.e.*, dinicotinic acid, quinolinic acid, cinchomeronic acid and dipicolinic acid monohydrate, and shown that O–H···N or N^+–H···O hydrogen bonds play an important part in their crystal structures although the formation of the O–H···O hydrogen bond might also be plausible, as has been found in the isoelectronic benzenedicarboxylic acids.

As a part of the programme of topochemical studies on the role of π-electron interaction and hydrogen bonding in molecular stacking and overlap on crystal structure formation, the present paper reports the structure of the monohydrate molecular complex formed between 2,5-pyridinedicarboxylic acid (isocinchomeronic acid, ICA) and *N*,*N*-dimethylformamide (DMF).

Experimental

Crystals were obtained in the form of colourless hexagonal plates by slow evaporation from an ethanol solution of ICA to which was added a small amount of DMF. Since the crystals gradually decomposed, specimens cut from larger crystals were sealed in a film of adhesive agent Cemedine (Cemedine Co., Japan). The crystals used were 0·3 × 1·0 × 0·3 mm for the *b* axis, 0·1 × 0·2 × 0·3 and 0·4 × 0·5 × 0·5 mm for the *a* axis photographs. The cell dimensions were determined from rotation and Weissenberg photographs (Cu $K\alpha$, $\lambda=1{\cdot}5418$ Å). Intensity data were recorded on Weissenberg photographs for the layers $h0l$ to $h5l$ and $0kl$ to $4kl$. Out of about 2820 possible reflexions within the Cu $K\alpha$ sphere, 1683 independent non-zero reflexions were estimated visually. Lorentz–polarization and shape corrections were made, but no absorption correction was applied.

Crystal data

2,5-Pyridinedicarboxylic acid–*N*,*N*-dimethylformamide monohydrate, $(C_7H_5NO_4).(C_2H_7NO).(H_2O)$, F.W. 258·2. Monoclinic, $P2_1/a$, $a=14{\cdot}14$ (1), $b=7{\cdot}225$ (4), $c=12{\cdot}28$ (1) Å, $\beta=97{\cdot}3$ (1)°, $U=1244$ Å^3, $D_m=1{\cdot}38$ g cm^{-3} by flotation in CCl_4–xylene, $D_x=1{\cdot}378$ g cm^{-3} for $Z=4$, μ(Cu $K\alpha$) = 10·1 cm^{-1}, $F(000)=520$. Remarkable diffuse scattering was observed for reflexions 401 and 802 on the Weissenberg photographs.

Structure determination and refinement

The sharpened Patterson map gave the orientation and the location of the ICA molecule. A Fourier synthesis using 989 reflexions with $F_o/F_c<2{\cdot}5$ revealed all the heavy atoms in the asymmetric unit. A diagonal least-squares refinement with isotropic thermal parameters starting with $B=3{\cdot}5$ Å^2 gave an R value of 0·22. A difference Fourier map showed 14 peaks, but three were not identified definitely as H atoms. A block-diagonal least-squares refinement with anisotropic thermal parameters for non-hydrogen atoms reduced R to 0·101. At this stage, a disordered structure was postulated from the following considerations: (1) an isotropic thermal parameter of the formyl H showed an abnormal value, $-3{\cdot}0$ Å^2, (2) a difference Fourier synthesis gave the positions of all the H atoms but a high peak of about 1·4 e Å^{-3} at the position of the formyl H remained, as shown in Fig. 1, and (3) the C=O and C–H bond lengths in the formyl group were

---

* Part V: Kashino & Haisa (1975).

1·30 and 1·2 Å, respectively, which were longer than the expected values.

A disordered model was assumed in which O(5) was rotated by 180° around the C(11)–N(12) bond. Fourier maps calculated for the occupancy factors of the O atom at the O(5) site, $m=1\cdot0$ (normal) and 0·0 (an alternative), were compared. A plausible value for m of 0·756 was estimated from the following equation:

$$m/(1-m)=(\varrho_{m=1\cdot0}+\varrho_{m=0\cdot0})/(\varrho_{m=1\cdot0}+\varrho'_{m=0\cdot0})$$
$$=(7\cdot0+5\cdot4)/(1\cdot7+2\cdot3)=3\cdot1\ ,$$

where ϱ and ϱ' are electron densities at the O(5) and DO(5) sites respectively. With an isotropic thermal parameter for the O(5) and DO(5) atoms, conventional R values of 0·143, 0·141 and 0·144 were calculated for $m=0\cdot80$, 0·75 and 0·70 respectively.

With $m=0\cdot75$ and after the removal of $F(401)$, a least-squares refinement was carried out using the weighting scheme: $w=(F_{\max}/F_o)^2$ for $F_o>F_{\max}(=9\cdot0)$, and $w=1\cdot0$ for $0<F_o\le F_{\max}$. The contribution of the formyl H was not considered. The final R value was 0·082 for 1683 non-zero reflexions.*

The final atomic parameters are given in Tables 1 and 2. The atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1962). The computation was carried out on an NEAC 2200-500 computer at the Okayama University Computer Centre and an NEAC 2200-700 computer at the Computation Centre of Osaka University. The main programs used were *RSSFR*-4 and *RSDLS*-3 (Sakurai, 1967), *HBLS*-5 and *DAPH* (Ashida, 1973).

Table 2. *Final parameters of the hydrogen atoms with standard deviations in parentheses*

	x	y	z	B (Å^2)
H(1)	0·389 (2)	0·796 (5)	0·368 (2)	1·6 (0·7)
H(2)	0·342 (3)	0·595 (6)	0·516 (3)	4·6 (1·0)
H(3)	0·436 (2)	0·173 (5)	0·338 (3)	2·4 (0·7)
H(4)	0·502 (4)	0·698 (8)	0·035 (4)	7·7 (1·4)
H(5)	0·373 (3)	−0·035 (7)	0·550 (4)	7·3 (1·3)
H(6)	0·298 (4)	−0·442 (7)	0·734 (4)	7·1 (1·3)
H(7)	0·225 (3)	−0·448 (6)	0·826 (3)	4·6 (1·0)
H(8)	0·331 (3)	−0·458 (7)	0·860 (4)	6·6 (1·3)
H(9)	0·315 (5)	−0·174 (10)	0·986 (5)	11·3 (1·9)
H(10)	0·204 (4)	−0·136 (8)	0·943 (4)	8·8 (1·6)
H(11)	0·286 (4)	0·015 (8)	0·910 (4)	7·3 (1·3)
H(12)	0·474 (3)	0·088 (7)	0·098 (3)	5·6 (1·2)
H(13)	0·469 (3)	0·296 (7)	0·118 (4)	6·1 (1·2)

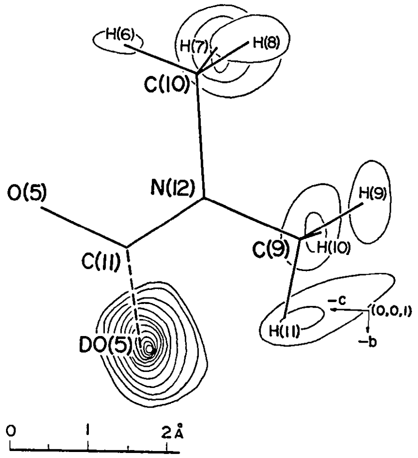

Fig. 1. Difference Fourier map at the stage of $R=0\cdot101$, showing the disorder of the formyl group. Contours are at intervals of 0·1 e Å^{-3} starting at 0·2 e Å^{-3}.

Table 1. *Final positional and thermal parameters* ($\times 10^4$) *with standard deviations in parentheses*

The anisotropic coefficients have the form $\exp(-\beta_{11}h^2-\beta_{22}k^2-\beta_{33}l^2-\beta_{12}hk-\beta_{13}hl-\beta_{23}kl)$.

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
N(1)	4468 (2)	4107 (4)	2602 (2)	68 (2)	181 (6)	62 (2)	−9 (5)	40 (3)	3 (5)
C(2)	4332 (2)	5924 (4)	2715 (2)	57 (2)	170 (7)	67 (2)	−18 (6)	25 (3)	−1 (6)
C(3)	3981 (3)	6680 (5)	3625 (3)	72 (2)	166 (7)	71 (2)	4 (7)	43 (4)	−10 (6)
C(4)	3775 (2)	5520 (5)	4452 (3)	63 (2)	198 (7)	65 (2)	−8 (7)	32 (3)	−34 (7)
C(5)	3915 (2)	3641 (5)	4348 (2)	54 (2)	187 (7)	57 (2)	−28 (6)	22 (3)	−12 (6)
C(6)	4263 (2)	2989 (5)	3420 (2)	66 (2)	165 (7)	64 (2)	−16 (6)	39 (3)	−3 (6)
C(7)	4566 (2)	7147 (5)	1802 (2)	67 (2)	173 (7)	67 (2)	−9 (6)	31 (3)	6 (6)
C(8)	3700 (2)	2356 (5)	5238 (2)	65 (2)	196 (7)	57 (2)	−16 (7)	41 (3)	1 (6)
O(1)	4852 (2)	6253 (4)	985 (2)	126 (2)	194 (6)	81 (2)	22 (6)	101 (4)	22 (5)
O(2)	4491 (2)	8803 (4)	1838 (2)	137 (3)	187 (6)	92 (2)	4 (6)	90 (4)	48 (6)
O(3)	3457 (2)	2942 (4)	6097 (2)	114 (2)	233 (6)	73 (2)	−3 (6)	84 (3)	−14 (5)
O(4)	3781 (2)	620 (4)	5020 (2)	128 (2)	190 (5)	85 (2)	−1 (6)	91 (4)	1 (5)
C(9)	2760 (4)	−1178 (8)	9222 (3)	106 (3)	444 (15)	73 (3)	11 (12)	41 (5)	−46 (11)
C(10)	2890 (3)	−3973 (7)	8091 (4)	110 (4)	289 (11)	107 (4)	−4 (10)	70 (6)	96 (10)
C(11)	3221 (3)	−932 (6)	7400 (3)	68 (2)	270 (10)	75 (3)	−7 (8)	18 (4)	43 (8)
N(12)	2952 (2)	−1980 (5)	8188 (2)	74 (2)	260 (7)	65 (2)	−1 (6)	30 (3)	4 (6)
O(5)	3420 (3)	−1601 (5)	6497 (2)	91 (2)	209 (7)	65 (2)	16 (7)	55 (4)	20 (6)
DO(5)	3242 (9)	715 (18)	7585 (10)	$B=6\cdot9\ (0\cdot3)$ Å^2					
O(6)	4719 (2)	2062 (3)	706 (2)	135 (3)	181 (5)	86 (2)	−14 (6)	93 (4)	26 (6)

---

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31244 (11 pp., 1microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Description and discussion of the structure

Molecular structure

The bond lengths and angles are shown in Fig. 2. The least-squares planes of the pyridine ring, the carboxyl groups and the DMF molecule are listed in Table 3. Some characteristic features of the molecular and crystal structures of pyridinedicarboxylic acids are compared in Table 4.

The pyridine ring has approximately C_{2v} symmetry. It should be noted that the difference in the N–C bond lengths increases as the difference in π-electron charge densities, q, at the substituted positions of the pyridine ring increases. The first dissociation of the carboxylic groups increases with the q value throughout the compounds. However, the protonation at the N atom increases in the first three compounds (Takusagawa, Hirotsu & Shimada, 1973*c*), but the extraordinary protonation is avoided by hydration in the last three. This situation is reflected in the C(2)–N(1)–C(6) angle, which increases in the top three, but becomes normal in the bottom two.

The carboxylic groups are coplanar with the pyridine ring in general, while a large twist occurs for the 3,4-acid in which intermolecular hydrogen bonds are in a spiral form. The two C–O bond lengths in each carboxyl group are distinctly different from each other, indicating that the acid is not a zwitterion. The smaller difference in the C–O bond lengths of C(8)–

Table 3. *Least-squares planes and deviations* (Å) *from the planes*
$X=ax+cz\cos\beta,\ Y=by,\ Z=cz\sin\beta$

(I) Pyridine ring					
$0{\cdot}8850X+0{\cdot}0987Y+0{\cdot}4550Z=6{\cdot}9724$					
N(1)*	0·003	C(8)	−0·009	H(3)	−0·01
C(2)*	−0·004	O(1)	0·043	H(4)	0·04
C(3)*	0·002	O(2)	−0·042	H(5)	0·04
C(4)*	−0·001	O(3)	−0·104	O(6)	0·624
C(5)*	0·001	O(4)	0·104	H(12)	0·57
C(6)*	−0·002	H(1)	0·01	H(13)	0·39
C(7)	−0·004	H(2)	0·12		
(II) 2-Carboxyl group					
$0{\cdot}8976X+0{\cdot}0680Y+0{\cdot}4356Z=6{\cdot}8524$					
C(2)*	0·000	N(1)	−0·038	O(6^{iv})	−0·007
C(7)*	−0·000	C(3)	0·052	H(12^{iv})	−0·08
O(1)*	0·000	H(4)	−0·00	H(13^{iv})	−0·21
O(2)*	0·000				
(III) 5-Carboxyl group					
$0{\cdot}9154X+0{\cdot}0272Y+0{\cdot}4017Z=6{\cdot}6498$					
C(5)*	0·001	O(4)*	0·001	H(5)	−0·08
C(8)*	−0·004	C(4)	0·110		
O(3)*	0·001	C(6)	−0·115		
(IV) DMF molecule					
$0{\cdot}9202X-0{\cdot}0953Y+0{\cdot}3797Z=6{\cdot}6122$					
C(9)*	−0·006	O(5)	−0·024	H(8)	−0·76
C(10)*	−0·006	DO(5)	0·020	H(9)	−0·75
C(11)*	−0·007	H(6)	0·08	H(10)	0·85
N(12)*	0·019	H(7)	0·74	H(11)	−0·00
				H(5)	−0·02

* Atoms with asterisks were used in the calculation of the planes.

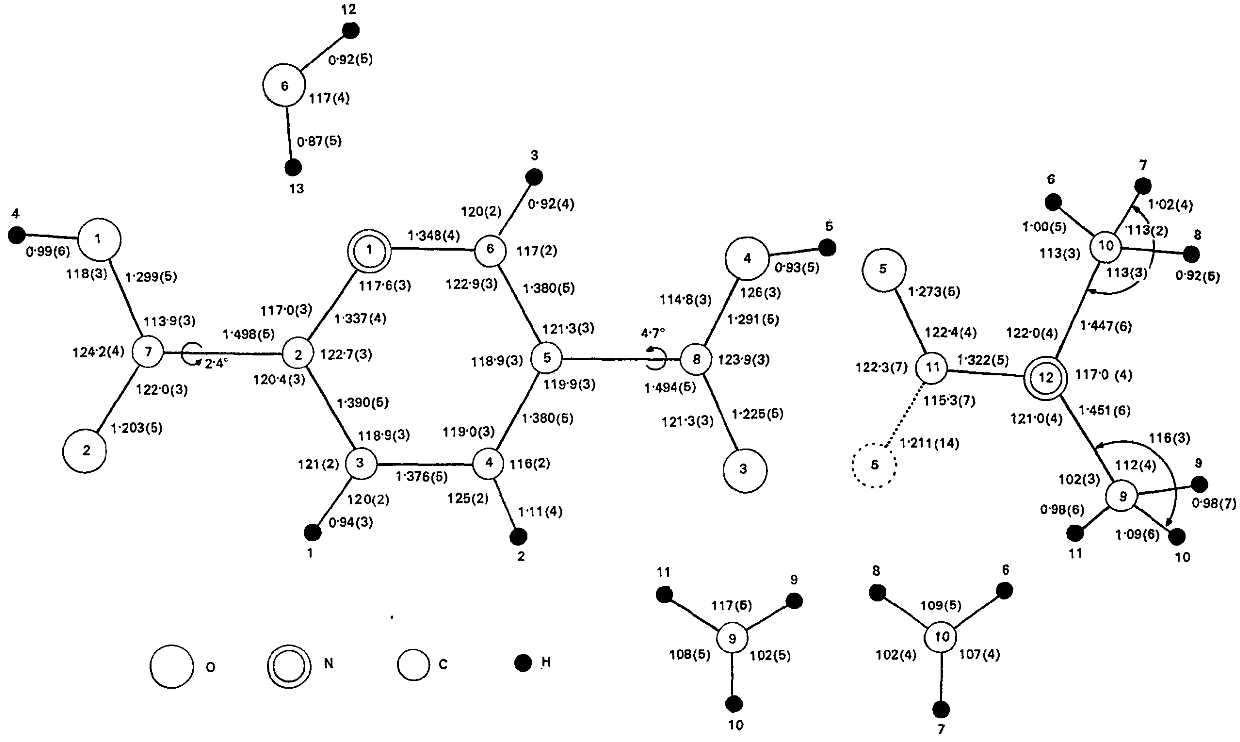

Fig. 2. Bond lengths (Å) and angles (°) along with numbering of atoms.

O(3) and C(8)–O(4) might be caused by the existence of disorder. In both carboxyl groups, the C–C–O angles associated with the shorter bonds are larger than those associated with the longer bonds, as is usually observed in carboxylic acids.

The DMF molecule is planar within the maximum deviation of 0·024 Å. The C(11)–O(5) length is longer than those in the other compounds as compared in Table 5.

Crystal structure

The crystal structure viewed down the *b* axis is shown in Fig. 3. All molecules lie approximately on the (401) planes. The crystals consist of molecular

Table 4. *Some characteristic features of the structures of pyridinedicarboxylic acids*

q: π-electron charge densities at the substituted positions of the pyridine ring calculated by the HMO method (Dewar, 1969). K_1: The first acid dissociation constant at 25°C (*International Critical Tables of Numerical Data, Physics, Chemistry and Technology*, 1929). τ: Torsion angles of the carboxylic groups with respect to the pyridine ring. *d*: Inter-ring spacing in the crystal.

Position of COOH	*q*	K_1 ($\times 10^3$)	Crystalline state	N–C (Å)	C–N–C (°)	τ (°)	*d* (Å)
3,5–	1·008, 1·008	1·45	neutral acid[a]	1·340, 1·342	119·8	6·7, −12·1	3·32 (1−*x*, 1−*y*, −*z*)
3,4–	1·008, 0·904	2·05	zwitter ion[b]	1·336, 1·349	122·3	−39·4, −73·0	–
2,3–	1·008, 0·855	2·95	zwitter ion[c]	1·326, 1·345	125·3	−8·3, 10·8	3·20 (1−*x*, −*y*, −*z*)
2,5–	1·008, 0·855	4·1	DMF hydrate[d]	1·348, 1·337	117·6	−2·4, −4·7	3·45 (1−*x*, 1−*y*, 1−*z*)
2,6–	0·855, 0·855	5·6	hydrate[e]	1·336, 1·338	116·8	−0·5, 0·8	3·35 ($\frac{1}{2}$−*x*, 1−*y*, $\frac{1}{2}$+*z*)
2,4–	0·904, 0·855	5·8	hydrate[f]	– –	–	– –	–

(*a*) Intermediate between neutral acid and zwitterion (Takusagawa, Hirotsu & Shimada, 1973*a*). (*b*) Takusagawa, Hirotsu & Shimada (1973*c*). (*c*) Takusagawa, Hirotsu & Shimada (1973*b*). (*d*) This work. (*e*) Takusagawa, Hirotsu & Shimada (1973*d*). (*f*) Meyer (1914). The structure has not been determined.

Table 5. *Comparison of bond lengths* (Å) *and angles* (°) *in the DMF molecule*

Figures in parentheses are the averaged values.

	(*a*)	(*b*)	(*c*)	(*d*)	(*e*)	(*f*)
C=O	1·23	1·235	1·211	1·220	1·273	1·219
$C_{carbonyl}$–N	1·34	1·317	1·327	1·308	1·322	1·366
C_{methyl}–N	(1·50)	(1·456)	(1·436)	(1·480)	(1·449)	1·459
C_{methyl}–N–C_{methyl}	120	117·2	120·4	119·4	117·0	–
C_{methyl}–N–$C_{carbonyl}$	(120)	(121·4)	(119·8)	(120·3)	(121·5)	121·4
N–C=O	124	124·2	125·4	127·2	122·4	124·6

(*a*) DMF–NaI complex (Gobillon, Piret & Van Meerssche, 1962). (*b*) Symmetrical cedrone (Beisler & Silverton, 1972). (*c*) 1:1 Complex of 1,7-diacetoxy-2,4,6-trinitro-2,4,6-triazaheptane and DMF (Cobbledick & Small, 1973). (*d*) μ-*N*,*N*′-Bis-(2-dimethylaminoethyl) oxamidatodiisothiocyanate–bisdimethylformamidecopper(II) (Yoshino & Nowacki, 1974). (*e*) This work. (*f*) *N*-Methylformamide (Kitano & Kuchitsu, 1974).

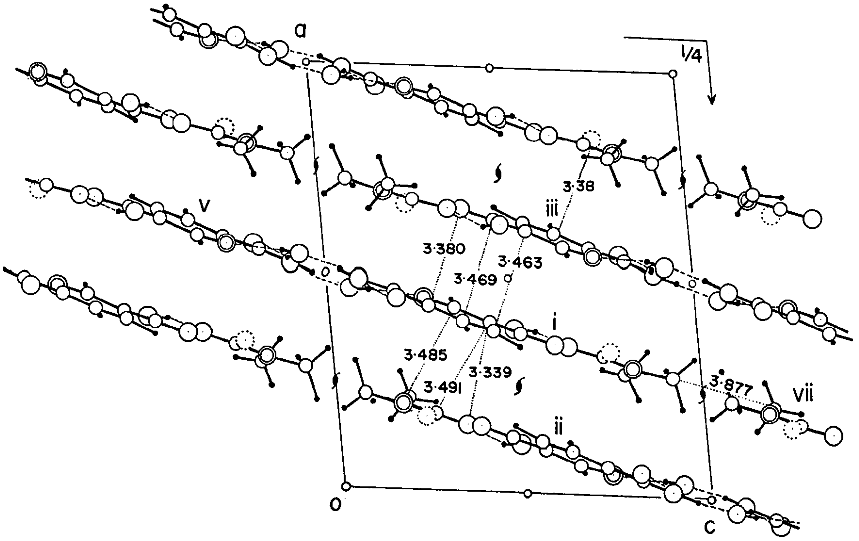

Fig. 3. The crystal structure viewed down the *b* axis. Symmetry code :(i) *x*,*y*,*z*; (ii) $\frac{1}{2}-x,\frac{1}{2}+y,1-z$; (iii) $1-x,1-y,1-z$; (v) $1-x,2-y,-z$; (vii) $\frac{1}{2}-x,\frac{1}{2}+y,2-z$.

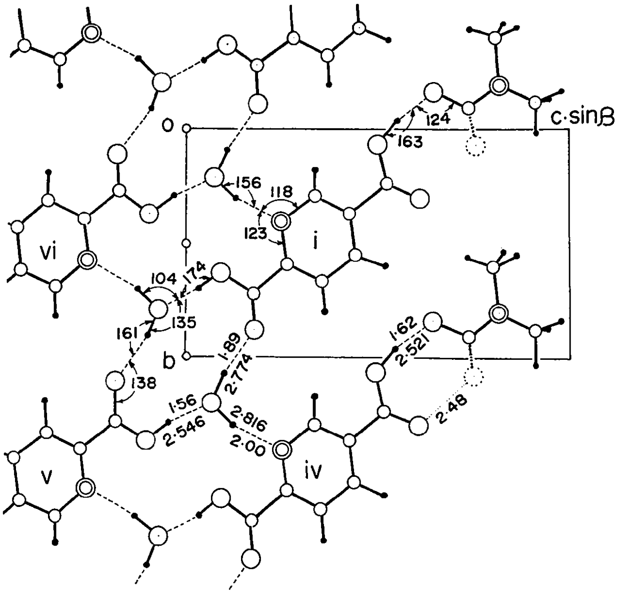

Fig. 4. The hydrogen-bond system viewed down the *a* axis. Symmetry code: (i) x,y,z; (iv) $x,1+y,z$; (v) $1-x,2-y,-z$; (vi) $1-x,1-y,-z$.

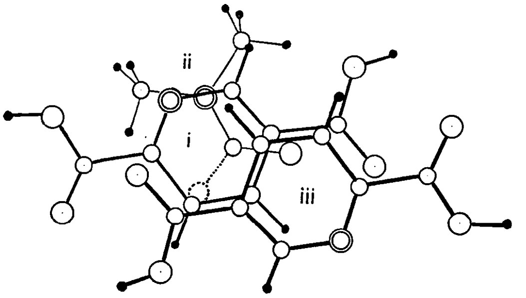

Fig. 5. Molecular overlapping. Symmetry code as in Fig. 3.

layers, one pair of which (i,ii) is related by the two-fold screw axis at $x=\frac{1}{4}$ and $z=\frac{1}{2}$, and the other (i,iii) by the centre of symmetry at $x=\frac{1}{2}$, $y=\frac{1}{2}$ and $z=\frac{1}{2}$.

The hydrogen-bond system is illustrated in Fig. 4. In each layer the ICA molecule is hydrogen bonded with the carbonyl group of the DMF molecule by the carboxylic group at the 5-position and with the adjacent ICA molecule, related by the centre of symmetry, by the carboxylic group at the 2-position through the two water molecules to form a dimeric unit of the compound. The units are linked by the hydrogen bond between the N atom of the pyridine ring and the hydroxyl group of the water to form a ribbon along **b**. Considering the C(7)–O(2)···H(12^{iv}) angle, one of the lone-pair electrons in the carbonyl O atom, O(2), seems to be directed toward a hydrogen-bond donor group. This is also the case for O(5) and N(1). The O(3)···DO(5) distance indicates hydrogen bonding.

Molecular overlapping is shown in Fig. 5. The ribbons are held together side-by-side by the dipole-dipole interaction of C(3^{i})···C(4^{i}) and C(5^{iii})···C(8^{iii}). Molecular overlap is observed at C(3), C(4), C(5) and C(8) in the present compound, whereas no large overlap is observed in the other acids. This is reflected in the inter-ring spacings in Table 4.

Although the sums of the *q*'s for the 2,3- and 2,5-acids are equal, the carboxylic groups in the former are closely arranged to form an intramolecular hydrogen bond whereas those in the latter are not. In the present compound, the DMF molecule contributes to the masking of the carboxylic group at the 5-position, and hence to the formation of the molecular sheet.

The diffuse scattering for reflexion 401 may result from a stacking fault in which layers having an O atom at the O(5) site and one at the DO(5) site occur with short-range order.

References

ASHIDA, T. (1973). *The Universal Crystallographic Computing System–Osaka*, The Computation Centre, Osaka Univ.

BEISLER, J. A. & SILVERTON, J. V. (1972). *Acta Cryst.* **B28**, 298–304.

COBBLEDICK, R. E. & SMALL, R. W. H. (1973). *Acta Cryst.* **B29**, 1659–1666.

DEWAR, M. J. S. (1969). *The Molecular Orbital Theory of Organic Chemistry.* New York: McGraw-Hill.

GOBILLON, Y., PIRET, P. & VAN MEERSSCHE, M. (1962). *Bull. Soc. Chim. Fr.* pp. 551–555.

International Critical Tables of Numerical Data, Physics, Chemistry and Technology (1929). Vol. VI. New York: McGraw-Hill.

International Tables for X-ray Crystallography (1962). Vol. III, pp. 202–203. Birmingham: Kynoch Press.

KASHINO, S. & HAISA, M. (1975). *Acta Cryst.* **B31**, 1819–1822.

KITANO, M. & KUCHITSU, K. (1974). *Bull. Chem. Soc. Japan*, **47**, 631–634.

MEYER, H. (1914). *Mh. Chem.* **35**, 189–206.

SAKURAI, T. (1967). *The Universal Crystallographic Computing Program System.* The Crystallographic Society of Japan.

TAKUSAGAWA, F., HIROTSU, K. & SHIMADA, A. (1973*a*). *Bull. Chem. Soc. Japan*, **46**, 2292–2299.

TAKUSAGAWA, F., HIROTSU, K. & SHIMADA, A. (1973*b*). *Bull. Chem. Soc. Japan*, **46**, 2372–2380.

TAKUSAGAWA, F., HIROTSU, K. & SHIMADA, A. (1973*c*). *Bull. Chem. Soc. Japan*, **46**, 2669–2675.

TAKUSAGAWA, F., HIROTSU, K. & SHIMADA, A. (1973*d*). *Bull. Chem. Soc. Japan*, **46**, 2020–2027.

YOSHINO, A. & NOWACKI, W. (1974). *Z. Kristallogr.* **139**, 337–350