Acta Cryst. (1976). B**32**, 1925

Isonicotinic Acid

BY FUSAO TAKUSAGAWA AND AKIRA SHIMADA*

Department of Chemistry, Faculty of Science, Osaka City University, Sugimoto-cho, Sumiyoshi-ku, Osaka 558, *Japan*

(*Received* 24 *November* 1975; *accepted* 19 *February* 1976)

Abstract. $C_6H_5NO_2$, M.W. 123·11, triclinic, space group $P\bar{1}$; $a=7{\cdot}231$ (1), $b=7{\cdot}469$ (1), $c=6{\cdot}392$ (1) Å; $\alpha=114{\cdot}88$ (2), $\beta=106{\cdot}19$ (1), $\gamma=103{\cdot}66$ (2)° (from double-radius Weissenberg photographs with Al calibration lines); $D_o=1{\cdot}47$, $D_c=1{\cdot}488$ g cm^{-3}; $\mu=9{\cdot}75$ cm^{-1}. The final residual $R=0{\cdot}056$. The molecule takes the neutral form in the crystal. Molecules related by translation along the b axis are linked in infinite chains by means of O–H···N hydrogen bonds with an O···N distance of 2·582 (3) Å. These chains are joined by the weak C–H···O hydrogen bonds to form a sheet parallel to the (100) plane.

Introduction. The crystal was obtained in the form of a colourless plate by recrystallization from an aqueous solution. Intensity data were collected by multiple-film equi-inclination integrating Weissenberg methods, with the intensities obtained by comparison with a standard strip from the crystal. Nickel-filtered Cu $K\alpha$ radiation was used for data collection. The crystal used for intensity collection had approximate dimensions: 0·4 × 0·3 × 0·3 mm. 1159 reflexions were investigated, with 1070 observed and 89 treated as unobserved. Lorentz and polarization corrections were applied to the intensities. Spot size, absorption and extinction corrections were not applied. The intensities were placed on a common scale by using the procedure proposed by Hamilton, Rollett & Sparks (1965).

The structure was solved by inspecting the sharpened Patterson map. Successful solution of the structure led to the assignment of $P\bar{1}$ as the appropriate space group. All hydrogen atoms were found in a difference Fourier map. The structural parameters of the atoms including isotropic hydrogen were refined in a full-matrix least-squares procedure, minimizing the function $\sum w(|F_o|-|F_c|)^2$, where: $w=1{\cdot}0/[10(|F_o|-1{\cdot}0)^2+1{\cdot}0]$ for $|F_o|\le 1{\cdot}0$; and $w=1{\cdot}0/[(|F_o|-1{\cdot}0)^2+1{\cdot}0]$ for $|F_o|\ge 1{\cdot}0$. The final agreement indices are: $R=\sum(|F_o|-|F_c|)/\sum|F_o|=0{\cdot}056$ (0·053 without $F_o=0{\cdot}0$); and $R_w=[\sum w(|F_o|-|F_c|)^2/\sum w|F_o|^2]^{1/2}=0{\cdot}081$ (0·080 without $F_o=0{\cdot}0$). The atomic scattering factors were obtained from *International Tables for X-ray Crystallography* (1962), except for hydrogen, for which the scattering factor of Stewart, Davidson & Simpson (1965) was used.† The positional and thermal parameters are listed in Table 1.

Discussion. This work is a part of a series of studies on the O–H···N hydrogen bonding in carboxylic acids with an aromatic six-membered ring.

Bond lengths and angles are given in Fig. 1. The isonicotinic acid molecule can take either the neutral or the zwitterion form. However, the position of the hydrogen atom in the difference Fourier map makes it evident that the molecule takes the neutral form in the crystal. This is supported by the fact that the difference between the two C–O bond lengths is 0·079 (3) Å and the C–N–C bond angle is 118·9 (2)°.

The pyridine ring is essentially planar, and the maximum deviation of the ring atoms from the least-squares plane is 0·004 Å. The C–N–C bond angle of 118·9 (2)° is larger than those of non-protonated pyridine compounds (~117°) (Singh, 1965). This may

* Deceased 5 August, 1973.

† A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31693 (8 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 1. *The final positional and thermal parameters*

The parameters and standard deviations (in parentheses) for the last significant digit of the non-hydrogen atoms are multiplied by 10^4. The expression for the thermal parameter is $\exp[-(B_{11}h^2+\ldots+B_{12}hk+\ldots)]$.

	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
N(1)	2375 (2)	4307 (2)	3117 (2)	272 (6)	190 (6)	398 (10)	226 (4)	277 (6)	297 (6)
C(2)	1981 (2)	3634 (2)	4640 (3)	314 (8)	207 (8)	382 (12)	266 (6)	350 (8)	267 (8)
C(3)	2063 (2)	1732 (2)	4406 (3)	293 (8)	202 (6)	376 (12)	236 (6)	329 (8)	295 (8)
C(4)	2553 (2)	464 (2)	2504 (2)	212 (6)	182 (8)	354 (12)	174 (6)	221 (6)	242 (8)
C(5)	2960 (2)	1162 (2)	928 (3)	263 (8)	220 (8)	381 (12)	240 (6)	325 (6)	305 (8)
C(6)	2863 (2)	3097 (2)	1295 (3)	288 (8)	229 (8)	398 (12)	239 (6)	322 (8)	373 (8)
C(7)	2651 (2)	−1628 (2)	2163 (3)	244 (6)	187 (6)	365 (10)	213 (4)	268 (6)	255 (6)
O(1)	2184 (2)	−2108 (2)	3727 (2)	458 (8)	237 (6)	526 (12)	432 (6)	615 (8)	468 (6)
O(2)	3149 (2)	−2705 (2)	560 (2)	472 (8)	259 (6)	545 (12)	457 (6)	660 (8)	421 (8)

Table 1 (*cont.*)

The positional parameters of the hydrogen atoms are multiplied by 10^3.

	x	y	z	B
H(1)	163 (3)	455 (4)	600 (4)	5·7 (4)
H(2)	186 (3)	141 (3)	560 (4)	4·9 (4)
H(3)	332 (3)	38 (3)	−51 (4)	5·2 (4)
H(4)	307 (3)	359 (4)	20 (4)	5·5 (4)
H(5)	222 (4)	−361 (5)	347 (5)	9·2 (8)

Table 2. *Distances and angles of hydrogen bonds*

X—H$\cdots$$Y$	$X\cdots Y$	H$\cdots$$Y$	X–H$\cdots$$Y$
O(1)–H(5)$\cdots$N(1)^{i}	2·582 (3) Å	1·51 (4) Å	177 (3)°
C(2)–H(1)$\cdots$O(2)^{ii}	3·306 (3)	2·46 (3)	143 (3)
C(6)–H(4)$\cdots$O(2)^{iii}	3·329 (3)	2·66 (3)	128 (3)

Symmetry code

Superscript			
i	x	$y-1$	z
ii	x	$y+1$	$z+1$
iii	x	$y+1$	z

be caused by the stronger interaction between the H(5) and N(1) atoms in a hydrogen bond. The dihedral angle between the planes of the pyridine and the carboxyl group is 2·0°.

Fig. 2 gives a stereoscopic illustration of the molecular arrangement. The distances and angles of the hydrogen bonds are listed in Table 2. The molecules are arranged in layers parallel to the (100) plane. The chains along the *b* axis, consisting of molecules linked by O–H$\cdots$N hydrogen bonds on the same plane, are joined by weak C–H$\cdots$O hydrogen bonds to form a sheet. There is no hydrogen bond between the sheets, which are packed by van der Waals forces.

Studies of O–H$\cdots$N hydrogen bonds reveal two categories of hydrogen bonds, N^+–H$\cdots$$O^-$ and O–H$\cdots$N, between the carboxyl group and nitrogen atom on an aromatic six-membered ring. The former is found in the pyridine–dicarboxylic acids: quinolinic acid (Takusagawa, Hirotsu & Shimada, 1973) and cinchomeronic acid (Takusagawa, Hirotsu & Shimada, 1973), while the latter is found in the following monocarboxylic acids: nicotinic acid (Wright & King, 1953) and pyrazinic acid (Takusagawa, Higuchi, Shimada, Tamura & Sasada, 1974). A type intermediate between the two exists in dinicotinic acid (Takusagawa, Hirotsu & Shimada, 1973). In isonicotinic acid, the position of the hydrogen atom and the dimensions of the carboxyl group indicate the latter type of hydrogen bond. Analysis of the molecular packing in monocarboxylic acids reveals that in all but picolinic acid (Takusagawa & Shimada, 1973), the carbonyl oxygen atom is surrounded by two hydrogen atoms at distances close enough to indicate appreciable C–H$\cdots$O interactions. These could be considered as weak C–H$\cdots$O hydrogen bonds or attractive van der Waals contacts. In dicarboxylic acids on the other hand, there is never more than one hydrogen in the vicinity of the oxygen atoms. These observations suggest that two weak C–H$\cdots$O hydrogen bonds could play a part in inhibiting the formation of a zwitterion.

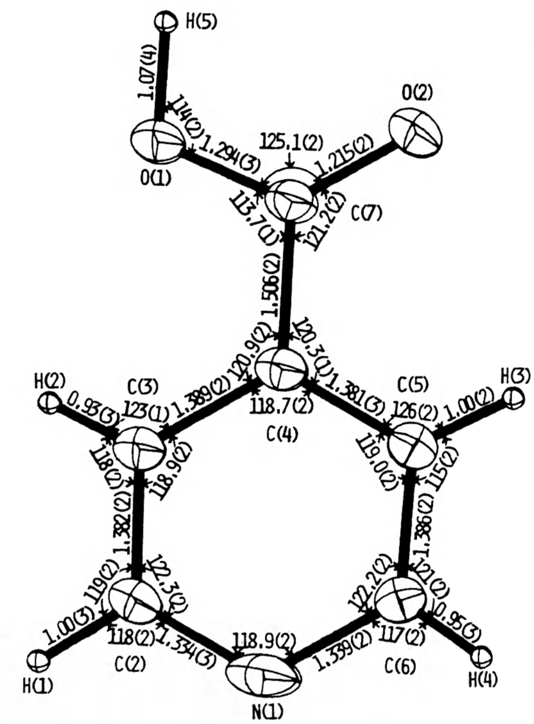

Fig. 1. Bond lengths and angles for isonicotinic acid.

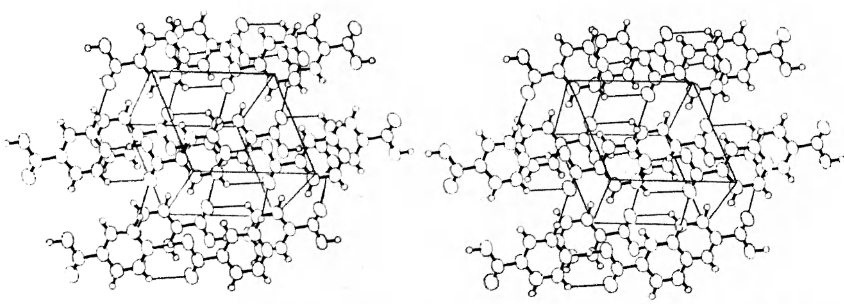

Fig. 2. The crystal structure of isonicotinic acid as viewed down the *a* axis. The *b* axis is horizontal.

All calculations were performed on a FACOM 270-30 computer at the Computer Center of Osaka City University, using programs *UNICS* (Sakurai, 1967) and *SHILCS* (Hirotsu, Yoshioka, Takusagawa & Nakatsu, 1974).

References

HAMILTON, W. C., ROLLETT, J. S. & SPARKS, R. A. (1965). *Acta Cryst.* **18**, 129–130.

HIROTSU, K., YOSHIOKA, H., TAKUSAGAWA, F. & NAKATSU, K. (1974). *SHILCS*: *Shimada Laboratory Crystallographic Computing System* (I). Unpublished work.

International Tables for X-ray Crystallography (1962). Vol. III, pp. 201–207. Birmingham: Kynoch Press.

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

SINGH, C. (1965). *Acta Cryst.* **19**, 861–864.

STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.

TAKUSAGAWA, F., HIGUCHI, T., SHIMADA, A., TAMURA, C. & SASADA, Y. (1974). *Bull. Chem. Soc. Japan*, **47**, 1409–1413.

TAKUSAGAWA, F., HIROTSU, K. & SHIMADA, A. (1973). *Bull. Chem. Soc. Japan*, **46**, 2020–2037, 2292–2299, 2372–2380, 2669–2675.

TAKUSAGAWA, F. & SHIMADA, A. (1973). *Chem. Lett.* pp. 1089–1090.

WRIGHT, W. B. & KING, G. S. D. (1953). *Acta Cryst.* **6**, 305–317.

Acta Cryst. (1976). B**32**, 1927

Pentamethyl 11,11a-Dihydro-9-oxo-9*H*,10*H*-cyclobuta[4,5]cyclopenta[3,4]pyrrolo[1,2-*a*]quinoline-7,8,10,11,11a-pentacarboxylate

BY PATRICK J. ABBOTT AND R. MORRIN ACHESON

*Department of Biochemistry, South Parks Road, Oxford OX*1 3*QU*, *England*

R. A. FORDER AND D. J. WATKIN*

Chemical Crystallography Laboratory, 9 *Parks Road*, *Oxford OX*1 3*PD*, *England*

AND J. R. CARRUTHERS

Oxford University Computing Laboratory, 19 *Banbury Road*, *Oxford*, *England*

(*Received* 9 *February* 1976; *accepted* 6 *March* 1976)

Abstract. The title compound was obtained as an uncharacterized reaction product. Its structure has provided a key to the interpretation of the NMR spectra of related products. $C_{27}H_{23}NO_{11}$, $M=537$; monoclinic, $P2_1/b$ (C_{2h}^5, No. 14); $a=10{\cdot}41$ (1), $b=14{\cdot}31$ (1), $c=16{\cdot}89$ (2) Å, $\gamma=91{\cdot}91$ (5)°, $U=2514{\cdot}7$ Å^3; $D_x=1{\cdot}40$, $D_c=1{\cdot}36$ g cm^{-3}, $Z=4$; Cu$K\alpha=1{\cdot}5418$ Å, $\mu=9{\cdot}6$ cm^{-1}; $R=0{\cdot}065$.

Introduction The purple material (m.p. 227–230°C) crystallized from methanol as thick six-sided plates. A crystal (0·3 × 0·3 × 0·15 mm) was mounted perpendicular to the smallest face. The setting angles of 25 reflexions measured each side of the incident beam were used in a least-squares calculation to give the cell parameters and orientation matrix. An absorption profile (North, Phillips & Mathews, 1968) was measured for the 600 reflexion ($I_{max}:I_{min}=1{\cdot}4:1$) and used to correct the intensities which were measured with an $\omega/2\theta$ scan and a modified ordinate analysis method (Watson, Shotton, Cox & Muirhead, 1970). Cu $K\alpha$ radiation was used with Zr/Y balanced filters for $\theta<30°$ and a Zr β-filter for $30°<\theta<60°$. 3813 reflexions were observed yielding 2207 with $I\geq 3\sigma(I)$. The structure was solved by direct methods (Sheldrick, 1973) and refined by least squares (block 1: all x,y,z; 2: all U_{ii}'s; 3: all U_{ij}'s; 4: scale factor and dummy overall temperature factor) (Carruthers, 1975). H atoms were ignored. The final R was 0·065 and the Hamilton weighted R 0·087. Weights were calculated from $w=1/\{4{\cdot}8\times T[0]'(x)+7{\cdot}4\times T[1]'(x)+3{\cdot}4\times T[2]'(x)+0{\cdot}7\times T[3]'(x)\}$ where $T[i]'$ are modified Chebychev coefficients and $x=F_o/F_o(\max)$ (Rollett, 1965). Scattering factors were taken from *International Tables for X-ray Crystallography* (1962). The final atomic parameters are listed in Tables 1 and 2 and the bond lengths and angles (with estimated standard deviations computed from the full variance–covariance matrix) in Tables 3 and 4. Fig. 1 shows the molecular geometry.†

* To whom correspondence should be addressed.

† A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31718 (18 pp., 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.