The Crystal Structure of α-Pyridoin, 1,2-Di-2-pyridylethenediol-1,2*

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The crystal structure of α-pyridoin (1, 2-di-2-pyridylethenediol-1, 2) has been determined from the three-dimensional intensity data and refined by the least-squares method with anisotropic thermal parameters. The positions of all the hydrogen atoms were found by a three-dimensional difference Fourier synthesis and included in the refinements. The crystal is monoclinic, space group $C2/c$, and $a = 16 \cdot 62$, $b = 4 \cdot 72$, $c = 13 \cdot 18$ Å and $\beta = 100 \cdot 1°$. The molecule possesses a center of symmetry and has a *trans* configuration around the central C–C double bond. Within the accuracy of the analysis, the molecule is planar. There are two intramolecular O–H...N hydrogen bonds in the molecule; they are between the enolic OH groups and the heterocyclic nitrogen atoms; the distances O..N, O–H and H..N are 2·599, 0·88 and 1·78 Å respectively. Thus, the molecule is not an α-hydroxyketone, but has an enediol structure stabilized through two intramolecular hydrogen bonds.

Introduction

The crystal structure of 1,2-di-2-pyridylethanedione (2,2′-pyridil, II) has been reported by the first two of the present authors (Hirokawa & Ashida, 1961); the structure is rather unusual in that it exhibits a plane-to-plane stacking made by four almost parallel pyridine rings. The present study on α-pyridoin was initiated in order to obtain further crystal chemical information on aromatic structures. Moreover, the structure analysis can no doubt settle the problem of molecular configuration of the compound. α-Pyridoin is obtained from pyridine-2-aldehyde by a benzoin condensation (Harries & Lenart, 1915). The substance is not stable in the air and is easily oxidized to 2,2′-pyridil. The molecular structure of α-pyridoin has been a subject of studies of several chemists. Mathes, Sauermilch & Klein (1951) suggested that the molecule could be an enediol. Infrared spectroscopic data (Lüttke & Marsen, 1953; Hensel, 1953) and a series of chemical reactions (Cramer, 1953; Cramer & Krum, 1953) suggest that it behaves like an enediol stabilized through formation of two intramolecular hydrogen bonds between the enolic OH groups and the heterocyclic nitrogen atoms. Eistert & Munder (1955) suggested a symmetrical planar *trans* form for the molecule based on some chemical reactions and ultraviolet spectroscopic data. Buehler, Addleburg & Glenn (1955) have shown that the formation of two intramolecular hydrogen bonds contributes to the stability of enediols. Thus, these works show that the molecular structure of α-pyridoin is represented by

(I)   (II)   (III)

(IV)
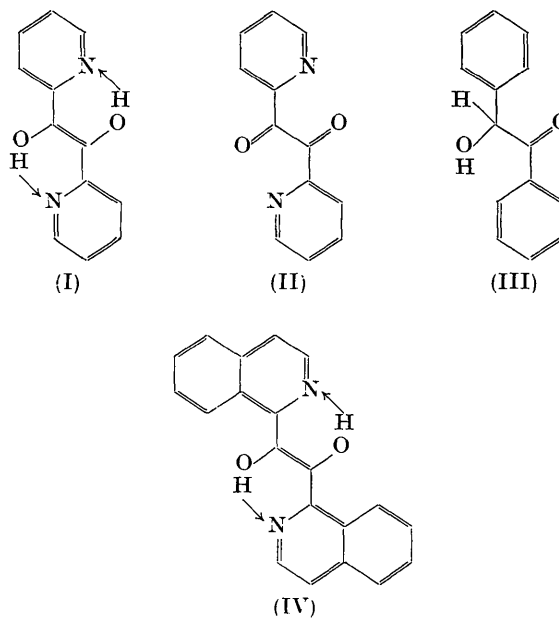
formula (I) and is not similar to that of benzoin (III) or furoin, both of which exist as α-hydroxy ketones (Lüttke & Marsen, 1953). A similar conclusion has been also reported for α-quinaldoin (IV) (Buehler & Harris, 1950).

A full three-dimensional structure analysis of α-pyridoin is discussed in the present paper. The results will include clarification of the molecular configuration, the packing of molecules in the crystal and the nature of the intramolecular O–H · · · N hydrogen bond.

Experimental

Well-developed crystals of α-pyridoin, $C_{12}H_{10}N_2O_2$, m.p. 156 °C, were kindly supplied by Prof. D. Oda of the Defense Academy. The crystals are deep reddish-orange plates elongated along the monoclinic b axis. The unit-cell dimensions were obtained from Weissenberg photographs about the principal axes. They are:

$$a = 16.62 \pm 0.02, \quad b = 4.72 \pm 0.01,$$
$$c = 13.18 \pm 0.02 \text{ Å}; \quad \beta = 100.1 \pm 0.3°.$$

The density of the crystal measured by the flotation method is 1·39 g.cm^{-3}; the value may be compared to the calculated value of 1·40 g.cm^{-3} by assuming four molecules in a unit-cell of the above dimension.

The space group was found to be either Cc or $C2/c$, from the systematic absences of the following reflections: hkl for $h+k=2n+1$ and $h0l$ for $l=2n+1$. A statistical investigation of the intensity data by the method of Howells, Phillips & Rogers (1950) suggested that the crystal is centrosymmetrical, and $C2/c$ was adopted for the space group throughout the study. The choice was later substantiated by the complete analysis of the structure.

Three-dimensional intensity data were obtained from equi-inclination Weissenberg photographs, with the use of Cu $K\alpha$ radiation. As the crystals were not stable in the air, they were coated with thin films of vinyl acetate, and rotated around the b axis ($k=0$ to 3) and the c axis ($l=0$ to 8). More than 90% of the total reflections within the limiting sphere for Cu $K\alpha$ radiation were recorded. Intensities were estimated visually by comparison with a standard scale. They were corrected for the Lorentz and polarization factors, and the effect of elongations of reflections in higher layer photographs was also taken into account by the method of Phillips (1956). The crystals used were so small that no absorption corrections were deemed necessary.

Structure determination

Since the crystal belongs to $C2/c$ and the number of molecules in a unit cell is four, the molecule has to conform with the symmetry requirement of the space group; e.g. a center of symmetry or a twofold axis.

The structure determination was initiated by calculating the projection of a sharpened Patterson function on (010), which is shown in Fig. 1(c). The interpretation of the map was straightforward by using the method adopted by Cochran for his study on the structure of salicylic acid (Cochran, 1953; Lipson & Cochran, 1957). A planar model for the molecule (Fig. 1(a)) was assumed, in which all the bond distances and bond angles made by the non-hydrogen atoms were supposed to be 1·4 Å and 120° respectively; it was also assumed that all the atoms
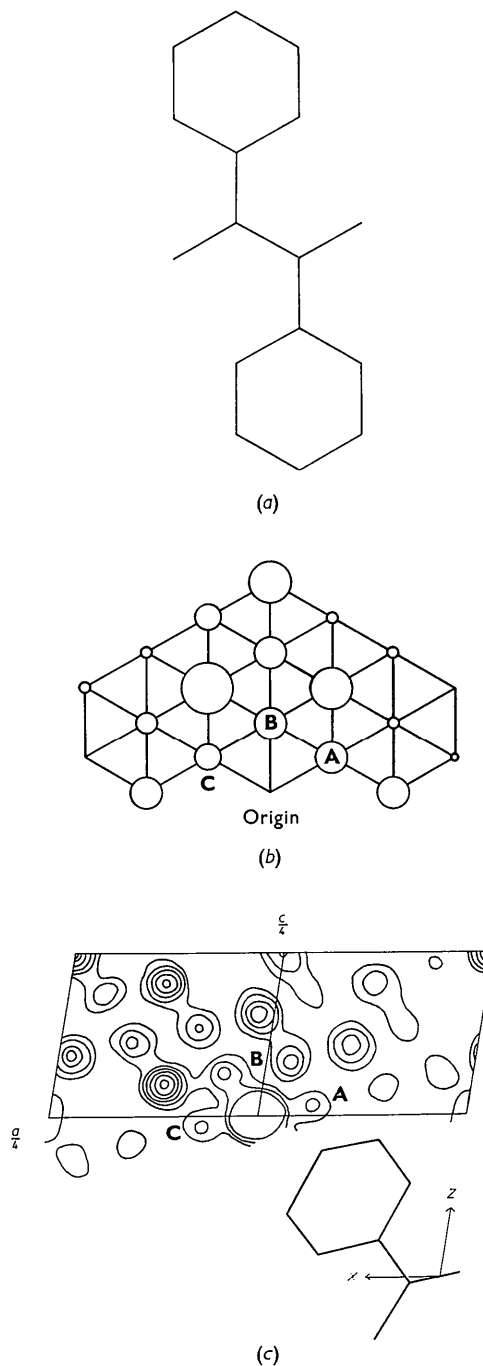

Fig. 1. Derivation of the trial structure from the projection of the Patterson function on (010). (a) The structure assumed for α-pyridoin. (b) The vector set for (a). Only the vectors shorter than 4·2 Å are collected, and the sizes of circles are in proportion to their weights. (c) The sharpened Patterson function projected on (010). Contours are drawn at equal intervals on an arbitrary scale, and those at the origin are removed. The peaks marked by the symbols A, B and C correspond respectively to the vectors A, B and C in the vector set in (b). The model shown in (c) is the structure thus derived.

have an equivalent scattering power. A vector map for this model is shown in Fig. 1(b), where the sizes of circles indicate the weights of vectors; vectors longer than 4·2 Å are not included. Since the b axis of the crystal is short, the structure should exhibit well-resolved molecules when viewed along this axis. Thus, the distribution of peaks near the origin of the Patterson function projected on (010) should correspond to the vector set shown in Fig. 1(b). The symmetry of the present crystal requires all the molecules in a unit cell to have the same orientation in this projection, and this fact made the interpretation much simpler than that for salicylic acid. The vector set and the Patterson function were compared with each other and a good fit of the vector set on the Patterson function could be obtained in the way shown in Fig. 1(b) and (c). The middle point of the molecule was placed at a center of symmetry in the b axis projection, and the structure factors $F(h0l)$ calculated on this basis showed fairly good agreement with those observed. Then the projection of the electron density function on (010) was synthesized, and showed a well-resolved structure clearly. The y coordinates of these atoms were then obtained by the projection of the electron-density function on (001) and also by bounded projections of the density along the a axis. A systematic study of the calculated structure factors placed the molecules at centers of symmetry rather than on twofold axes.

The atomic coordinates of the non-hydrogen atoms thus obtained were then refined by the full-matrix least-squares method with anisotropic temperature factors assigned to each atom. After several cycles, the refinements of the structure seemed to have slowed down; at this stage, a three-dimensional $(F_o - F_c)$ synthesis was made and the positions of all the hydrogen atoms were established. These hydrogen coordinates were then included in subsequent refinements; only isotropic temperature factors were assigned to account for their thermal vibration. A sudden drop in the error index, R, was observed and after three cycles of refinements, no significant changes in parameters were observed $(R = 0·083)$.* The computation was done on an IBM 7094 computer at the IBM Research Center with programs written by one of the authors (Okaya, 1962). The final atomic coordinates and the vibration factors are listed in Table 1. The three-dimensional electron-density function and an $(F_o - F_{O+N+C})$ synthesis were calculated and are shown in Fig. 2. It might be worthwhile to mention that at the final stage the omission of the hydrogen contribution in the structure-factor calculation raises the R index to 0·113 with several changes in the signs of structure factors.

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* A table comparing the observed and calculated structure factors may be obtained from the authors on request.

Table 1. *Atomic coordinates and temperature factors*

(a) Atomic coordinates (in fraction of cell edges) and their standard deviations in 10^{-4} Å

	x	σ(x)	y	σ(y)	z	σ(z)
C(1)	0·08192	16	0·27042	22	0·05965	19
C(2)	0·15301	18	0·39503	27	0·03572	22
C(3)	0·19575	21	0·58759	29	0·10386	25
C(4)	0·16681	21	0·65534	31	0·19301	26
C(5)	0·09679	20	0·52340	28	0·21183	24
C(6)	0·03462	17	0·06524	22	−0·00991	20
N	0·05509	15	0·33529	21	0·14760	17
O	0·06637	14	0·01314	19	−0·09699	15
H(2)	0·170	211	0·350	277	−0·026	282
H(3)	0·248	248	0·683	349	0·089	295
H(4)	0·195	241	0·786	319	0·241	282
H(5)	0·073	210	0·575	254	0·271	262
H(O)	0·029	291	−0·107	361	−0·130	331

(b) Thermal parameters

Anisotropic temperature factors and corresponding thermal ellipsoids

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}	Principal axes (Å²)		
C(1)	0·003066	0·039577	0·004196	0·003138	0·001586	0·002921	3·97	2·68	2·94
C(2)	0·003586	0·053016	0·004697	−0·000722	0·002105	0·003081	4·82	2·91	3·90
C(3)	0·003681	0·061037	0·006410	−0·005950	0·000854	0·006315	6·39	3·48	3·95
C(4)	0·004163	0·055304	0·006293	−0·002350	−0·000128	−0·003006	5·34	3·49	5·00
C(5)	0·004115	0·054469	0·005040	0·000878	0·001200	−0·004120	5·10	3·23	4·38
C(6)	0·003237	0·040163	0·004030	0·002779	0·002674	0·001462	4·08	2·25	3·21
N	0·003571	0·048574	0·004824	−0·000189	0·002309	−0·002778	4·44	2·93	3·90
O	0·003957	0·054651	0·004656	−0·004232	0·004273	−0·003759	5·57	2·14	4·09

Isotropic temperature factors for hydrogen atoms (Å²)

H(2)	H(3)	H(4)	H(5)	H(O)
2·13	3·57	3·02	1·77	3·59

(a)

(b)
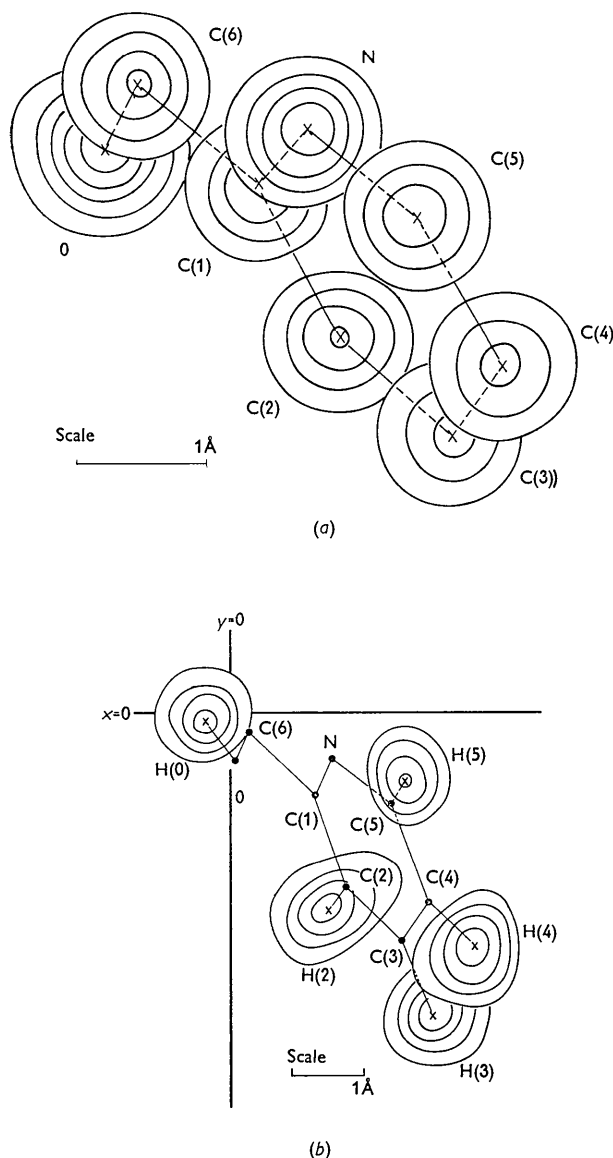
Fig. 2. (a) A composite diagram of the electron-density function showing the heavier atoms along the c axis. The contours are at intervals of 2 e.Å^{-3} starting with 2 e.Å^{-3}. (b) A composite diagram of the electron-density function associated with hydrogen atoms. The contours are drawn at equal intervals of 0·2 e.Å^{-3} starting with the same amount. The locations of the heavier atoms are also indicated.

Discussion

All the bond distances and angles and other important distances below 4·0 Å were evaluated on the IBM 7094 computer. They are shown in Fig. 3. The standard deviations of these values are also given there.

The equations of various planes in the molecule were evaluated by the least-squares method. For one-half of the molecule, the plane through the pyridine ring was evaluated. The deviations of the
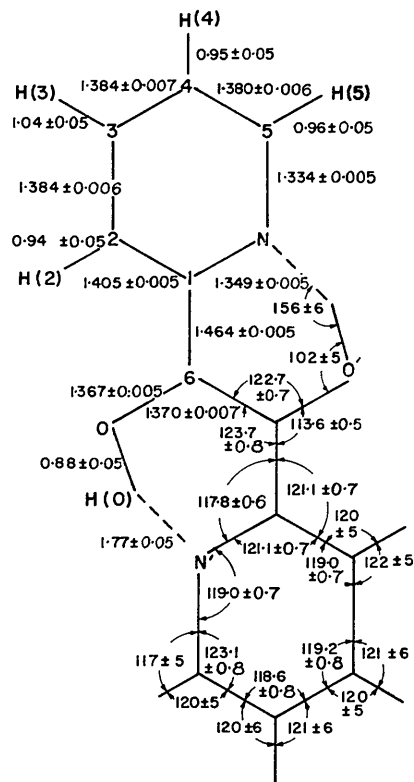

Fig. 3. The shape and size of the molecule (Å and degrees).

atoms in the ring are of the order of the standard deviations; whereas C(6) and O are off from the plane by 0·011 and 0·020 Å respectively. Then the planarity of the molecule as a whole was studied by evaluating
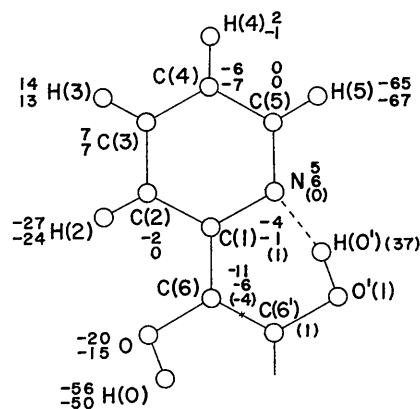

Fig. 4. The displacements (in 10^{-3} Å) of the atoms from the planes; the upper values from I (pyridine ring), the lower from II (the whole molecule) and those in parenthesis from III (the six membered ring made by the hydrogen bond). The equations of these planes are:

(I) $0.5495X - 0.7415Y + 0.3850Z = 0.0046$
(II) $0.5490X - 0.7424Y + 0.3840Z = 0.0$
(III) $0.5535X - 0.7418Y + 0.3786Z = 0.0010$

where $X = ax \sin \beta$, $Y = by$ and $Z = cz + ax \cos \beta$.

the plane through the rings and C(6) and C(6′); the two oxygen atoms were excluded from the calculation. The result as shown in Fig. 4 demonstrates that the molecule as a whole is again planar with the two oxygen atoms away from the plane by only 0·015 Å. It should be noted here that owing to large standard deviations in their atomic coordinates, none of the hydrogen atoms was included in the plane evaluations. The molecule is therefore roughly of symmetry $2/m$ with a mirror on the molecular plane and a twofold axis perpendicular to the plane through the center of symmetry. A *trans* configuration around the central C–C bond is observed. Such a planar *trans* configuration is, no doubt, stable and common to many conjugated systems (Pauling, 1960).

The shape of the pyridine ring is very close to that reported for many substances. No significant differences were found between the dimensions of the pyridine ring of the present crystal and those of 2,2′-pyridil (Hirokawa & Ashida, 1961). The mean values of C–C, C–N, and the angles C–N–C, N–C–C, and C–C–C are 1·388, 1·342 Å, 118·9, 122·1, and 118·9°, respectively. By microwave spectroscopy (Bak, Hansen & Rastrup-Andersen, 1954) the corresponding values in pyridine are 1·395, 1·340 Å and 116·7, 124·0 and 118·4°, respectively. Therefore, the shape and the size of the pyridine ring in α-pyridoin are almost the same as in the free pyridine molecule, regardless of the presence of a side chain. Some other examples of pyridine derivatives also exhibit similar configurations for the pyridine rings (*e.g.* nicotinic acid (Wright & King, 1953), nicotinamide (Wright & King, 1954), and so on). The C–H bond distances were found to be 0·94–1·04 Å, and these distances seem to be shorter than the accepted value which has been found by other methods (Sutton, 1958). Similar contraction of the lengths of bonds containing hydrogen atoms is usually found by the X-ray method (*e.g.* tetramethylenediammonium adipate (Hirokawa & Ashida, 1962), 2-amino-3-methylbenzoic acid (Brown & Marsh, 1963) and for a collection of C–H distances, see Jensen (1962)). The O–H bond distance, 0·88 Å, found in the enol group seems to show a similar tendency. Tomiie (1958) has made a quantum-mechanical treatment of such contraction of X–H bonds as obtained by the X-ray method.

The bond distances C(1)–C(6), 1·464 Å and C(6)–C(6′), 1·370 Å, are in good agreement with those observed in other conjugated systems. Some of the reported values are: 1·46 and 1·35 Å for butadiene-1,3 (Schomaker & Pauling, 1939), 1·45 and 1·33 Å for *trans*-stilbene (Robertson & Woodward, 1937), 1·45 and 1·35 Å for 1,8-diphenyl-1,3,5,7-octatetraene (Drenth & Wiebenga, 1955), 1·46 and 1·36 Å for triclinic vitamin A (Stam & MacGillavry, 1963), and 1·47 and 1·33 Å for α-ionylidenecrotonic acid (Eichhorn & MacGillavry, 1959). In 2,2′-pyridil, 1·480 Å has been reported for the single C–C bonds in the conjugated system (Hirokawa & Ashida, 1961). The

C–O bond distance (1·367 Å) found in the present crystal is much shorter than the distance of the normal C–O single bond (1·43 Å); possible resonance structures readily explain this double-bond character.

Several X-ray studies have been published on intramolecular hydrogen bonds of O–H $\cdots$ O or N–H $\cdots$ O types in crystals. However, few examples have been reported on O–H $\cdots$ N hydrogen bonds; the present crystals will be a rare example for the intramolecular hydrogen bonds of this type. The hydrogen bond completes an almost coplanar six membered ring. The plane through this ring was evaluated from the coordinates of C(1), C(6), C(6′), O′ and N; the deviations of the atoms from the plane are also shown in Fig. 4. The angles C(6)–O–N′ and N′–O–H(O) are 86·1 and 16°, respectively, and the hydrogen atom H(O) is off the O $\cdots$ N line by 0·24 Å. Thus, the deviation from the linearity of the O–H $\cdots$ N bond may be significant. The observed O $\cdots$ N distance, 2·599 Å, is somewhat shorter than the usual O–H $\cdots$ N bond distances of intermolecular type (about 2·8 Å (Pimentel & McClellan, 1960; Wallwork, 1962)); however, it may not be unusual for such intramolecular hydrogen bonds. Further studies on compounds with intramolecular O–H $\cdots$ N bonds are necessary to correlate the hydrogen bond distances with the non-linearity of the bond. Thus in the crystal,
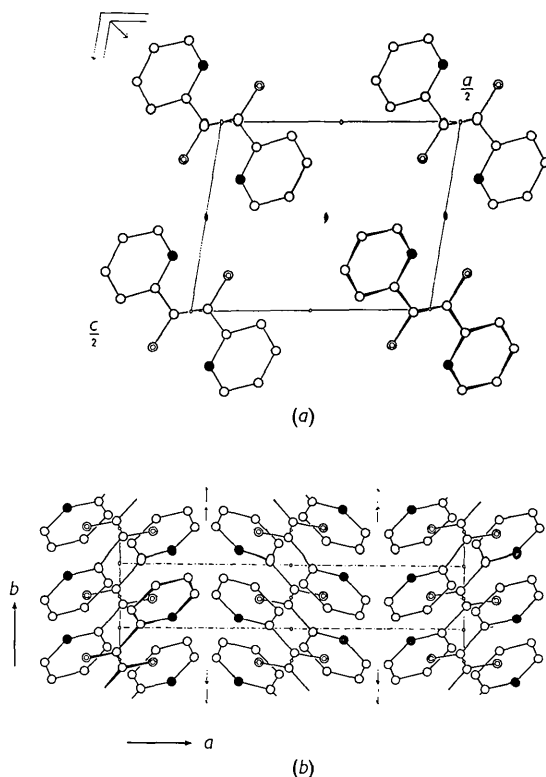

(a)

(b)

Fig. 5. (a) The crystal structure projected on (010). Only a quarter of a unit cell is shown. (b) The structure projected on (001). Open circles carbon; closed circles nitrogen; double circles oxygen.

α-pyridoin exists as a centrosymmetrical, coplanar enediol with two intramolecular hydrogen bonds as suggested by the several authors mentioned above. The intense color (reddish-orange) of the crystal may be attributed to the structure of the molecule thus described. Then the name hydroxy-2-pyridylmethyl-2-pyridyl ketone adopted by Chemical Abstracts should not be retained, but 1,2-di-2-pyridylethenediol-1,2 may be used instead.

The arrangement of the molecules in the crystal is shown in Fig. 5. There are only normal van der Waal's contacts among the molecules as shown by the following nearest intermolecular contacts: the oxygen atom has two neighboring atoms, H(4) and C(5) of the molecule related to the first by the c-glide at $y = \frac{1}{2}$, the separations being 2·63 and 3·441 Å, respectively.

In contrast to the structure of 2,2'-pyridil, the molecular packing in the structure is a normal one and no plane-to-plane stacking of rings is found. Therefore, the structure of 2,2'-pyridil still remains as a rather unusual example of molecular packing.

We are grateful to Prof. D. Oda of the Defense Academy for supplying the crystals of α-pyridoin and also for his continued interest.

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Short Communications

Contributions intended for publication under this heading should be expressly so marked; they should not exceed about 1000 words; they should be forwarded in the usual way to the appropriate Co-editor; they will be published as speedily as possible. Publication will be quicker if the contributions are without illustrations.

Zur Struktur des Phosphophyllits, Zn₂Fe(PO₄)₂.4H₂O. Korrektur.

Von W. KLEBER und E.

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Die Tabelle der Atomkoordinaten unserer Arbeit über den Phosphophyllit (Kleber, Liebau & Piatkowiak, 1961) enthält zwei Fehler. Der mit 0,39 angegebene y-Wert für O_{IV} muss heissen 0,11 (= 0,50 − 0,39); der mit 0,17 angegebene y-Wert für $(H_2O)_{II}$ muss heissen 0,83 (= 1,00 − 0,17).

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