Acta Cryst. (1961). **14**, 774

The Crystal Structure of 2,2'-Pyridil

BY SAKUTARO HIROKAWA AND TAMAICHI ASHIDA

Department of Chemistry, Defence Academy, Yokosuka, Japan

(*Received* 7 *September* 1960)

2,2'-Pyridil, $C_{12}H_8N_2O_2$, crystallizes in the monoclinic system with $a=6{\cdot}41$, $b=13{\cdot}03$, $c=12{\cdot}79$ Å and $\beta=99{\cdot}5°$; the space group is $P2_1/n$. The unit cell contains four chemical units.

The structure was determined by using three-dimensional X-ray data. Refinement of the atomic coordinates was made by the least-squares method on the IBM 704 machine.

The molecular structure is not meso-ionic but totally covalent; the molecule consists of two planes each of which includes a pyridine ring, a carbonyl group and its adjacent carbon atom, the angle between the two planes being 83°. There are found no unusually short intermolecular atomic distances which indicate strong interacting forces between molecules, though the crystals are not easily sublimed. The characteristic feature of the crystal structure is a plane-to-plane stacking made by four almost parallel pyridine rings.

Introduction

The chemical structure of quinaldil $C_{20}H_{12}N_2O_2$ has been a subject of many discussions. Brown & Hammick (1950) suggested a meso-ionic formula for the substance; however, the formula was not supported by chemical or spectroscopic studies (Buehler & Harris, 1950, 1952), nor by a preliminary X-ray work (Davies & Powell, 1951). So it seemed worth-while to complete a structure analysis of the substance or its related compounds from a view-point of their molecular structures.

2,2'-Pyridil has an analogous structural formula to quinaldil, and is much simpler than the latter. Therefore, it was used by the present authors to decide whether the structure is meso-ionic or not. Since the substance is rather less volatile compared with similar compounds, the presence of a strong interaction among the molecules is anticipated; therefore it might be interesting to compare the crystal structure of this compound with those of other molecular compounds.

Crystallographic data

2,2'-Pyridil $C_{12}H_8N_2O_2$ was kindly supplied by Prof. D. Oda of the Defence Academy. The material was recrystallized from an ethanol solution. The pale yellow crystals thus obtained showed that they belong to the monoclinic system. The cell dimensions were obtained from oscillation and Weissenberg photographs around the three principal axes, using Cu $K\alpha$ radiation. They are:

$$a=6{\cdot}41\pm0{\cdot}02,\ b=13{\cdot}03\pm0{\cdot}02,\ c=12{\cdot}79\pm0{\cdot}03,\ \beta=99{\cdot}5\pm0{\cdot}5°.$$

A density of 1·36 g.cm.$^{-3}$ was found for the crystals by flotation. With this value, the number of molecules per cell was calculated to be 4, 0. The space group was determined to be $P2_1/n$.

Equi-inclination Weissenberg photographs using the usual multiple-film technique were taken about the a- ($h=0$ to 3) and the b-axis ($k=0$ to 7). About 80% of the total reflections (including very weak ones) within the limiting sphere of Cu $K\alpha$ were recorded. Intensities were estimated visually by comparison with standard scales. Since even the largest dimension of any of the crystals used was less than 0·5 mm., no correction was made for absorption. After being corrected for Lorentz and polarization factors, the intensities were roughly converted to an absolute scale (Wilson, 1942).

Determination of the structure

At an early stage of the structure determination, it seemed worthwhile to apply the sign-determination method (Sayre, 1952) for $F(0kl)$'s, because the a-axis of the unit cell is rather short. However, the number of $F(0kl)$'s with unitary structure factors larger than 0·20 is small; only 37 signs out of 215 $F(0kl)$'s were tentatively given by this method. An approximate electron-density projection $\varrho(y,z)$ was calculated using the $F(0kl)$'s, the signs of which were thus determined; the resulted map was far from being able to distinguish any atom in the molecule. After several cycles of successive syntheses of $\varrho(y,z)$, this trial was given up, because no considerable improvement was obtained other than a rough lay-out of the molecules in the unit cell. Therefore, an attempt was made to solve the structure *via* interpretation of the three-dimensional Patterson function. $P(u,v,w)$ was computed using all the observed $F^2(hkl)$'s at intervals of 1/30, 1/60 and 1/60 along the a-, b- and c-axes, respectively. The interpretation of the diagram thus obtained was not difficult, because the lay-out of the molecules had already been given by the approximate electron-density projection along the a-axis. It did not take long to identify all the peaks closer than 3·6 Å from the origin of the Patterson space. The third step of the structure determination was the bounded-projection method proposed by Booth (1945). Structure factors were calculated using the atomic coordinates roughly determined by the interpretation of the three-dimensional Patterson function. The bounded projections used here were $B_0^{1/4}$, $B_{-1/8}^{1/8}$ and $B_{1/8}^{3/8}$ along both the *b*- and *c*-axes.

Table 1. 2,2′-*Pyridil*

Atomic coordinates and their standard deviations (in units of $10^{-4}\times$ cell edges) and temperature factors B (in 10^{-16} cm.^{2})

Atoms	x	$\sigma(x)$	y	$\sigma(y)$	z	$\sigma(z)$	B
N	5919	0018	1323	0008	2496	0006	6·11
C_1	5212	0024	0649	0010	1716	0009	6·88
C_2	3071	0025	0600	0011	1257	0009	7·18
C_3	1673	0026	1253	0011	1568	0009	7·67
C_4	2342	0024	1971	0010	2385	0009	6·96
C_5	4454	0019	1962	0008	2800	0007	5·27
C_6	5333	0020	2676	0008	3656	0007	5·64
O	4284	0017	3316	0007	4027	0006	7·20
N′	7079	0017	1273	0007	5178	0006	5·82
C_1'	7659	0023	0550	0010	5919	0008	6·47
C_2'	9755	0022	0467	0009	6372	0008	6·29
C_3'	1337	0022	1109	0009	6077	0008	6·26
C_4'	0665	0021	1853	0009	5301	0007	5·75
C_5'	8505	0018	1895	0008	4886	0008	4·85
C_6'	7708	0020	2647	0008	4043	0007	5·50
O′	8817	0017	3287	0007	3692	0006	7·18

Then a three-dimensional electron-density function was synthesized using the signs of $F(hkl)$'s based on the results of the bounded projections. Though *intra*- and *inter*molecular dimensions thus obtained seemed to be quite reasonable, the error index gave a value higher than 0·20; it was then considered desirable to proceed to the least-squares method. All the atomic coordinates—except those for hydrogen atoms—were subjected to least-squares refinement, using the automatic refinement program NYXR3 by Vand & Pepinsky (1958) on the IBM 704. After four refinement cycles, the error index decreased to 0·16. The final set of atomic coordinates and isotropic temperature factors is given in Table 1. It might be worthwhile to mention here that in view of the molecular configuration, the structure would have been refined better if anisotropic temperature factors had been used; however, since the present study aims mainly at an elucidation of the molecular structure, only isotropic temperature factors were used in the course of refinement. Standard deviations of the atomic coordinates have been assessed by the method of Cruickshank (1949) and are also listed in Table 1. A composite drawing of the electron-density function with sections perpendicular to the *b*-axis is shown in Fig. 1. Comparison between the observed and calculated structure factors is not given here. It may be available if required.

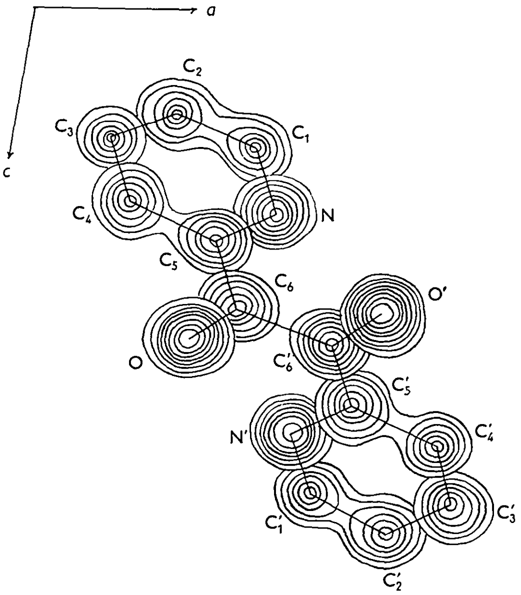


Fig. 1. Composite diagram of the three-dimensional electron-density function showing a molecule, viewed down the *b*-axis.

Description and discussion of the structure

Bond lengths and angles calculated from the coordinates listed in Table 1 are given in Tables 2(*a*) and (*b*)

Table 2. 2,2′-*Pyridil*

Bond lengths and angles

(*a*) Bond lengths and their standard deviations

C_5–C_6	$1{\cdot}47_7$ Å	$0{\cdot}01_5$ Å	C_5'–C_6'	$1{\cdot}48_3$ Å	$0{\cdot}01_5$ Å
C_6–O	$1{\cdot}21_5$	$0{\cdot}01_4$	C_6'–O′	$1{\cdot}22_8$	$0{\cdot}01_4$
C_6–C_6'	$1{\cdot}52_2$	$0{\cdot}01_5$			
	Ring I			Ring II	
N–C_1	$1{\cdot}34_9$ Å	$0{\cdot}01_6$ Å	N′–C_1'	$1{\cdot}34_3$ Å	$0{\cdot}01_6$ Å
N–C_5	$1{\cdot}35_9$	$0{\cdot}01_4$	N′–C_5'	$1{\cdot}32_1$	$0{\cdot}01_4$
C_1–C_2	$1{\cdot}40_3$	$0{\cdot}01_9$	C_1'–C_2'	$1{\cdot}37_7$	$0{\cdot}01_7$
C_2–C_3	$1{\cdot}34_3$	$0{\cdot}02_0$	C_2'–C_3'	$1{\cdot}41_3$	$0{\cdot}01_7$
C_3–C_4	$1{\cdot}41_4$	$0{\cdot}01_9$	C_3'–C_4'	$1{\cdot}40_3$	$0{\cdot}01_6$
C_4–C_5	$1{\cdot}37_1$	$0{\cdot}01_6$	C_4'–C_5'	$1{\cdot}40_1$	$0{\cdot}01_5$

(*b*) Bond angles and their standard deviations

C_5–C_6–O	123·7°	1·7°	C_5'–C_6'–O′	124·3°	1·7°
C_5–C_6–C_6'	117·7	1·6	C_5'–C_6'–C_6	117·3	1·6
C_6'–C_6–O	118·5	1·7	C_6–C_6'–O′	118·2	1·7
	Ring I			Ring II	
C_5–N–C_1	116·5°	1·8°	C_5'–N′–C_1'	120·5°	1·8°
N–C_1–C_2	121·7	2·0	N′–C_1'–C_2'	119·2	1·8
C_1–C_2–C_3	120·1	2·1	C_1'–C_2'–C_3'	122·4	2·0
C_2–C_3–C_4	120·1	2·2	C_2'–C_3'–C_4'	116·6	1·8
C_3–C_4–C_5	116·1	2·0	C_3'–C_4'–C_5'	117·7	1·7
C_4–C_5–N	125·4	1·9	C_4'–C_5'–N′	123·7	1·7
C_4–C_5–C_6	120·9	1·8	C_4'–C_5'–C_6'	120·1	1·7
N–C_5–C_6	113·7	1·5	N′–C_5'–C_6'	116·2	1·6

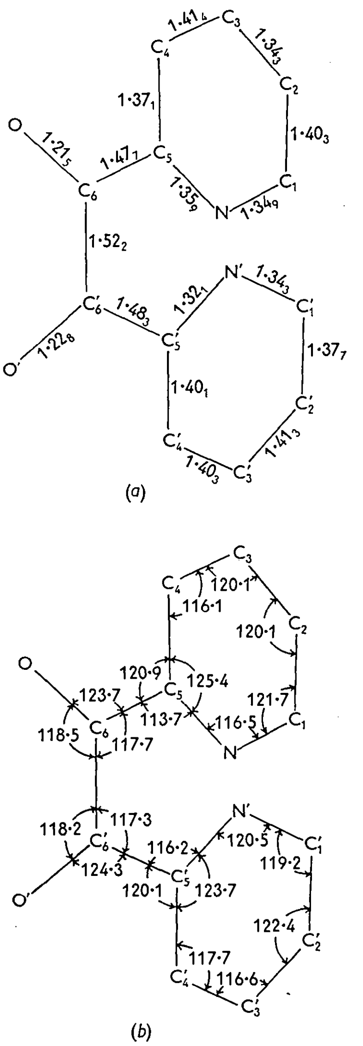
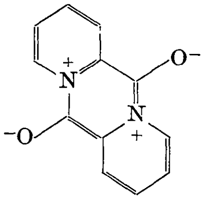


Fig. 2. (a) Bond distances in Å. (b) Bond angles in degrees.

together with their standard deviations; they are also shown in Figs. 2(a) and (b).

It is clear from Figs. 1 and 2 that the structure is totally covalent as in the case of quinaldil (Davies & Powell, 1951), and any meso-ionic structures, e.g.



and its resonance isomers are excluded at least in the crystalline state.

The shape of the pyridine rings is not significantly different from the value of 1·39 Å for C–C, 1·35–1·36 Å for C–N and 114–117° for C–N–C; these values were obtained by De More *et al.* (1954) from spectroscopic studies of pyridine. The value 1·34$_3$ Å found for C_2–C_3 bond will not be significant in view of the standard deviations for the coordinates of these atoms.

Equations of the planes, each of which includes the atoms forming a ring and its nearest neighbors (C_6 and C_6', respectively), were evaluated by the

Table 3. *Displacements of the atoms from the plane of the pyridine ring*

The plane I		The plane II	
N	−0·001 Å	N'	−0·004 Å
C_1	+0·005	C_1'	+0·005
C_2	−0·012	C_2'	+0·001
C_3	+0·007	C_3'	+0·004
C_4	+0·001	C_4'	−0·005
C_5	+0·002	C_5'	−0·014
C_6	−0·005	C_6'	+0·012
O	+0·012	O'	−0·010
C_6'	+0·053	C_6	−0·048

Table 4. *2,2'-Pyridil*

Intermolecular distances less than 4·0 Å

Plane I II'	Distances
N–C_3'	3·84 Å
N–C_4'	3·66
C_1–C_4'	3·76
C_2–O	3·71
C_2–C_4'	3·99
C_2–C_5'	3·74
C_2–C_6'	3·62
C_2–O'	3·69
C_3–C_6	3·93
C_3–O	3·40
C_3–N'	3·71
C_3–C_5'	3·56
C_3–C_6'	3·69
C_4–N'	3·62
C_4–C_1'	3·76
C_4–C_2'	3·98
C_4–C_4'	3·98
C_4–C_5'	3·71
C_5–C_2'	3·84
C_5–C_3'	3·68
C_5–C_4'	3·75
C_5–C_5'	3·97 Å
C_6–C_2'	3·76
C_6–C_3'	3·81
O–C_2'	3·81
O'–C_2'	3·96
O'–C_3'	3·55

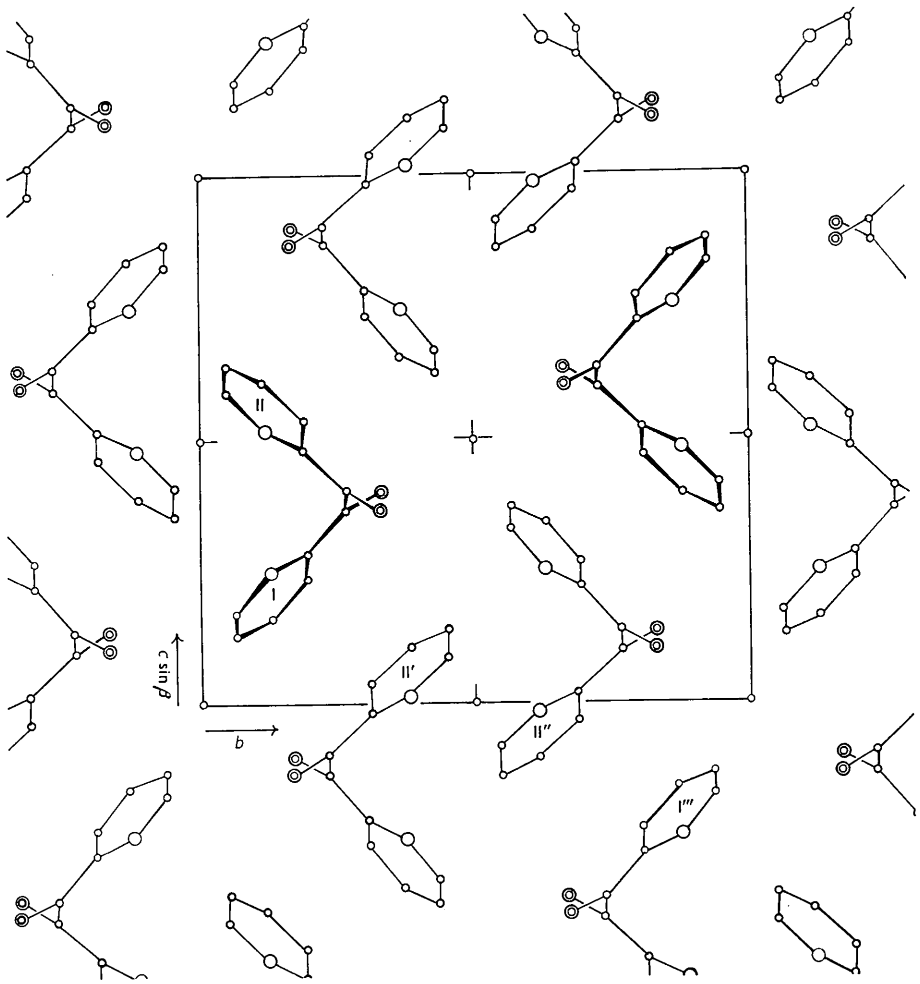
Plane II' II''	
N'–C_2'	3·81 Å
N'–C_3'	3·71
N'–C_1'*	3·93
C_1'–C_2'	3·83
C_1'–C_3'	3·49
C_1'–C_4'	3·74
C_2'–C_2'	3·78
C_2'–C_3'	3·71
C_2'–C_4'	3·69
C_2'–C_5'	3·73

Plane I I*	Distances
O–C_4'	3·59 Å
O–O'	3·46
C_4–O'	3·48

Plane I I''	
O–C_2	3·33 Å
O–C_3	3·93
O'–C_1*	3·20
O'–C_2*	3·61

Plane II' I''	Distances
C_1'–C_3	3·95 Å
C_1'–C_4	3·94
C_2'–N*	3·73
C_2'–C_1*	3·98
C_2'–C_3	3·69
C_2'–C_4	3·89
C_3'–N*	3·92

Asterisks (*) indicate that atoms are in the next cell.



(a)

Fig. 3. (*a*) The structure viewed down the *a*-axis.

method of least-squares. Let us call the plane closest to N, C_1, C_2, C_3, C_4, C_5 and C_6 plane I, and that to the corresponding primed atoms plane II. The equations are:

$$X+2{\cdot}298\,.\,Y-2{\cdot}359\,.\,Z+0{\cdot}200=0$$

for plane I, and

$$X-2{\cdot}465\,.\,Y-2{\cdot}677\,.\,Z+18{\cdot}114=0$$

for plane II, where

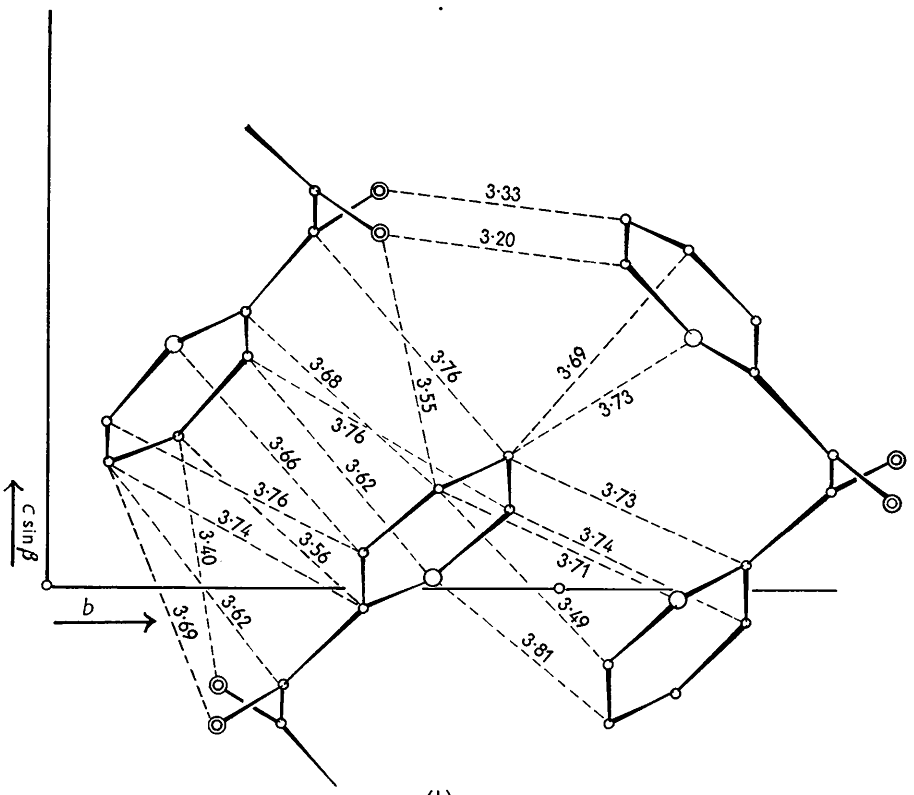
$$X=ax-cz\,.\cos\beta,\quad Y=by,\quad Z=cz\,.\sin\beta\;.$$

Displacements of the atoms from each evaluated planes are shown in Table 3, where the negative signs mean both the atom and the origin of the coordinate system lie on the same side of the plane. As is shown in Table 3, it can be safely assumed that each pyridine ring is planar within the limit of experimental errors. The atoms O and C_6' are shifted from plane I by 0·012 and 0·053 Å, respectively; the atoms O′ and C_6 by 0·010 and 0·048 Å, respectively from plane II. Therefore, the molecule consists of two planes, each of which contains a pyridine ring, a carbonyl group closer to the ring and a carbon atom of another carbonyl group; the two planes make an angle of 82·7° with each other.

The N and O are in the *trans*-relation around the C_5–C_6 bond. The same relation is held for N′ and O′. The O and O′ are in the *gauche*-form referring to the C_6–C_6' bond, being separated by a distance of 3·01 Å.

All intermolecular distances less than 4·0 Å are listed in Table 4. The structure viewed down the *a*-axis is shown in Fig. 3(*a*); in Fig. 3(*b*), several important van der Waals distances are shown. It should be noted that almost all shorter intermolecular distances are found around the stackings of the pyridine rings by holding reasonable separations for van der Waals contacts.

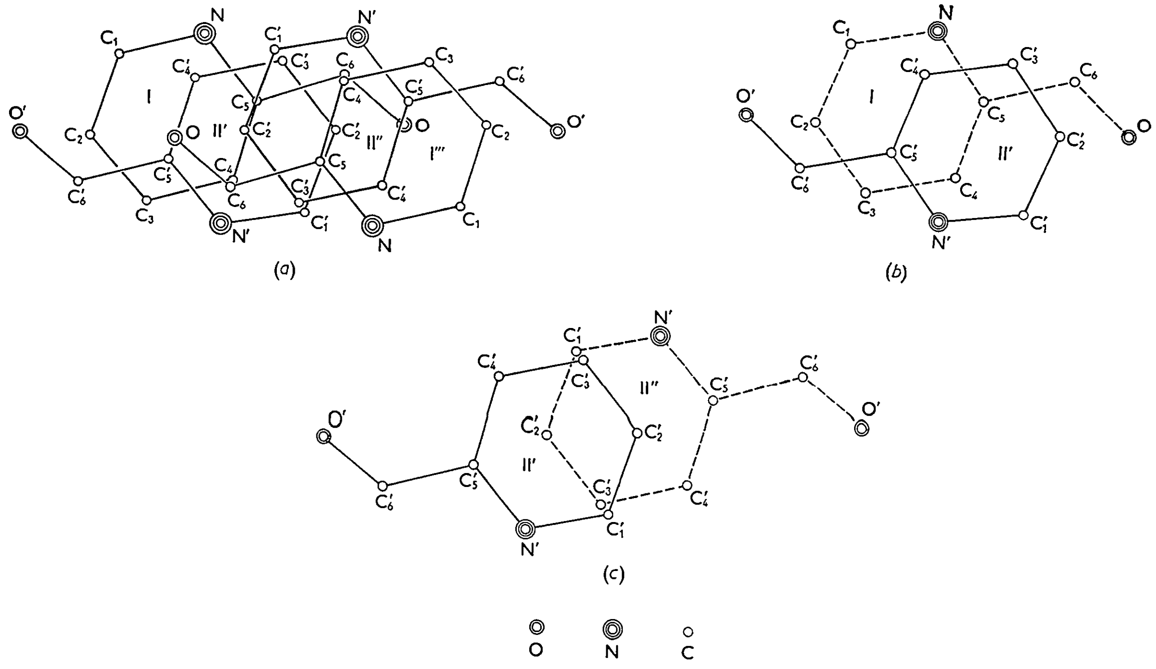
The crystals (m.p. 153 °C.) seem to be neither volatile nor easily sublimed, though quantitative-physico-



(b)

Fig. 3. (b) Enlargement of a part of Fig. 3(a). Several important van der Waals distances are shown.

chemical measurements were not tried on the substance. The predominant forces gathering the molecules in the crystal seem to be plane-to-plane interactions which might be similar to those found in the



(a) (b) (c)

Fig. 4. Projection of groups I, II″ and I‴ on II′, showing the off-sets of these groups. (a) All the three groups on II′. (b) I on II′. (c) II″ on I′.

crystals of phenoquinone (Harding & Wallwork, 1953), the chloranil–hexamethylbenzene complex (Harding & Wallwork, 1955) and quinhydrone (Matsuda *et al.*, 1958).

The intersecting angles between the planes I and II′ is calculated to be 2·0°, therefore they are approximately parallel to each other. The perpendicular distance between them is calculated to be 3·56 Å. This distance must be compared with those of 3·33 Å in phenoquinone and of 3·16 Å in quinhydrone; the latter two distances are definitely shorter than the usual van der Waals distances. The line connecting the center of the ring I to that of the II′ makes an angle of 70·7° with plane I.

As to the relation between II′ and II″, they are, as a matter of course, parallel, being separated by a perpendicular distance of 3·49 Å. A calculation for the angle between the line connecting the centers of both the rings II′ and II″ and each plane gives a value of 69·9°, showing again that the maximum overlapping of the two rings is not found. The distance between the centers of the rings I and II′ projected onto the plane I is 1·28 Å; a similar distance of 1·31 Å is found for the II′ and II″. The situation is also illustrated in Figs. 4(*a*), (*b*) and (*c*).

Thus the structural feature of 2,2′-pyridil is described in terms of columns each of which is built by approximately parallel four planes of pyridine rings (planes I, II′, II″ and I‴ in Fig. 3(*a*)).

The authors are extremely grateful to Prof. R. Pepinsky of The Pennsylvania State University for his kind permission of using the IBM 704 for the refinement of the structure. Extensive aids and advices of Prof. V. Vand and Dr F. M. Lovell of The Pennsylvania State University on the least-squares refinement procedure are sincerely appreciated. They are indebted to Prof. D. Oda of the Defence Academy who kindly supplied the material. They also wish to express their thanks to Prof. C. A. Buehler of The University of Tennessee who interested in this investigation.

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Acta Cryst. (1961). **14**, 779

Die Struktur des Silber-Polyphosphats $(AgPO_3)_x$

Von K. H. Jost

Institut für Strukturforschung der Deutschen Akademie der Wissenschaften zu Berlin,*
Berlin-Adlershof, Deutschland

(*Eingegangen am* 25. *Juli* 1960)

$(AgPO_3)_x$ crystallizes in space group $P2_1/n$ with cell dimensions

$$a=11{\cdot}86,\ b=6{\cdot}06,\ c=7{\cdot}31\ \text{Å},\ \beta=93{\cdot}5^\circ.$$

The structure was solved by the aid of direct methods. It contains helically arranged chains of PO_4 tetrahedra parallel to the *b* axis with 4 tetrahedra per turn. Each Ag atom has five oxygen neighbours.

Allgemeines

Von W. Wieker (nicht veröffentlicht) wurde durch Schmelzen von Silber-trimetaphosphat $Ag_3P_3O_9$ ein Silberpolyphosphat $(AgPO_3)_x$ dargestellt. Es kristallisiert in farblosen kurzen Nadeln der Dichte 4,65 g.cm.$^{-3}$. Elementarzelle, Raumgruppe und Zellinhalt sind

$$\begin{aligned} a &= 11{,}86 \pm 0{,}04\ \text{Å} \\ b &= 6{,}06 \pm 0{,}02\ \text{Å}\ \text{(Nadelachse)} \\ c &= 7{,}31 \pm 0{,}03\ \text{Å} \\ \beta &= 93{,}5^\circ \pm 0{,}5^\circ \end{aligned}$$

monoklin, Raumgruppe $P2_1/n$
8 Formeleinheiten $AgPO_3$ in der Elementarzelle
berechnete Dichte 4,73 g.cm.$^{-3}$.

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* Neue Adresse: Institut für Anorganische Chemie der Deutschen Akademie der Wissenschaften zu Berlin, Berlin-Adlershof, An der Rudower Chaussee.