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X-ray Studies of Pyridazino[4,5-*d*]pyridazine Derivatives.
II. The Structure of 1,4,5,8-Tetramethoxypyridazino[4,5-*d*]pyridazine

BY L. FANFANI AND P. F. ZANAZZI
Istituto di Mineralogia dell'Università di Perugia, Italy

AND C. SABELLI
Centro di Geochimica e Cristallochimica dei minerali del C.N.R., Istituto di Mineralogia dell'Università di Firenze, Italy

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1,4,5,8-Tetramethoxypyridazino[4,5-*d*]pyridazine, $C_{10}O_4N_4H_{12}$, is monoclinic, space group $P2_1/n$, with $a=4{\cdot}312$, $b=16{\cdot}826$, $c=7{\cdot}727$ Å, $\beta=101{\cdot}01°$ and $Z=2$. The crystals investigated are twinned with twinning plane (001). The crystal structure has been determined by a three-dimensional Patterson synthesis and refined to an R value of 0·057. The thermal motion was analysed in terms of rigid-body vibrations. The whole molecule is roughly planar and the dimensions of the heterocyclic ring are very similar to those occurring in pyridazino[4,5-*d*]pyridazine.

Introduction

The present study concerning the crystal structure of 1,4,5,8,-tetramethoxypyridazino[4,5-*d*]pyridazine (TMPP) is a part of a research program on the derivatives of pyridazino[4,5-*d*]pyridazine (PP). In the preceding paper (Sabelli & Zanazzi, 1972) the crystal structure of 2,6-dimethyl-4,8-dichloro-2*H*,6*H*-pyridazino-[4,5-*d*]pyridazin-1,5-dione (DDPPD) was described and the crystal structure of 1,5-dimethoxypyridazino[4,5-*d*] pyridazine is at present under investigation.

Experimental and structure determination

Crystals of TMPP were recently synthesized at the Istituto di Chimica Organica of Florence University. The crystals obtained by recrystallization from benzene are colourless elongated plates with m.p. 285 to 286°C (Adembri, De Sio, Nesi & Scotton, 1969). TMPP is monoclinic; lattice parameters were roughly determined by basal Weissenberg photographs and refined by the least-squares method applied to the reflexions with higher values of 2θ collected on $0kl$ and $h0l$ films, after calibration with Ag powder. Cell constants at room temperature are $a=4{\cdot}312(2)$, $b=16{\cdot}826(3)$, $c=7{\cdot}727(1)$ Å and $\beta=101{\cdot}01(2)°$; systematic extinctions indicate the space group $P2_1/n$. Calculated density assuming two molecules in the unit cell is 1·467 g,cm^{-3}, in agreement with the experimental value 1·46 g.cm^{-3}, measured by flotation in a mixture of carbon tetrachloride and chloroform.

All the crystals of TMPP subjected to X-ray investigation were seen to be twinned by the splitting of the diffraction effects on Weissenberg films. The arrangement of the spots has been explained taking into account the diffraction by two individuals having c^* and b^* axes antiparallel, while the angle between the a^* axes is 22·02° ($180°-2\beta^*$). Twinning in TMPP can be classified according Friedel (1926) as twinning by pseudo-merohedry with twin plane (001), threefold multiplicity and an obliquity of 20′. The resulting pseudo-orthorombic cell has the same a and b parameters as the monoclinic cell and $c=22{\cdot}819$ Å.

For the structural study, reciprocal lattice layers from $0kl$ to $3kl$ were recorded using the Weissenberg equi-inclination technique with Cu $K\alpha$ radiation. Intensities were measured with a microdensitometer. Because of twinning and lattice geometry, overlap of diffraction effects occurs on $0kl$ and $3kl$ layers; on the $0kl$ layer the reflexions $0kl$ of the A individual overlap the symmetry equivalent reflexions $0\bar{k}\bar{l}$ of the B individual; on the $3kl$ layer the reflexions having the index l of the A individual superpose those with index $l'=-(l+2)$ of the B individual. This fact makes a correction to the superimposed intensity data necessary. The correction was applied using the method described by Sabelli, Tangocci & Zanazzi (1969) which allows evaluation of the intensities of diffraction effects from a single individual when the volume ratio of the two individuals in the twin is known. This ratio was calculated using the data on $1kl$ and $2kl$ layers, where reflexions arising entirely from one or other of the individuals exist.

After the usual geometrical corrections, data were put on the same relative scale taking into account the exposure time of different layers. A total of 971 independent reflexions were recorded, 637 of them being in the measurable range. The unobserved reflexions were given a value just below the locally observable intensity.

Since $Z=2$, the molecule must lie with its symmetry centre on one of the special positions $\bar{1}$ of the $P2_1/n$ space group. The orientation of the molecules in the unit cell was obtained from a three-dimensional Patterson synthesis. Having solved the structure, it was refined, first with a series of electron density maps down to an R value of 0·19, and later using the least-squares method, employing the full-matrix program of Busing and Levy, adapted for the IBM 7090 computer by Stewart (1964). The following weighting scheme was used: $\sqrt{w}=1$ for observed reflexions having $F \leq 4F_{\min}$ and for unobserved reflexions with $F_{\text{calc}} > F_{\min}$; $\sqrt{w}=4F_{\min}/F$, for reflexions having $F > 4F_{\min}$; $\sqrt{w}=0$ for the unobserved reflexions with $F_{\text{calc}} \leq F_{\min}$.

Six reflexions presumably affected by extinction were excluded from calculations. The R value reduced to 0·08 after two isotropic and two anisotropic cycles of refinement. At this stage a Fourier difference map revealed the positions of hydrogen atoms of the methyl groups. A further refinement cycle was then carried out with the contribution of all atoms. A value of 5 Å^2 was fixed for the thermal parameters of the hydrogen atoms. The refinement was then stopped and R reached the final value, 0·057. Atomic parameters with standard deviations and thermal parameters are listed in Tables 1 and 2. Observed and calculated structure factors are given in Table 3. The atomic scattering factors used for O,N,C and H are listed in *International Tables for X-ray Crystallography* (1962).

Table 1. *Fractional atomic parameters with their standard deviations*

	x	y	z
O(1)	0·2835 (6)	0·0321 (1)	−0·3187 (3)
O(2)	−0·3231 (6)	0·1162 (1)	0·1998 (3)
N(1)	0·0428 (7)	0·1240 (1)	−0·1722 (3)
N(2)	−0·1078 (7)	0·1461 (1)	−0·0389 (3)
C(1)	0·1317 (8)	0·0506 (2)	−0·1860 (3)
C(2)	−0·1672 (8)	0·0937 (2)	0·0725 (4)
C(3)	−0·0763 (7)	0·0108 (2)	0·0670 (4)
C(4)	0·3170 (13)	0·0946 (2)	−0·4409 (5)
C(5)	−0·3805 (12)	0·2001 (2)	0·2138 (5)
H(1)	0·479 (12)	0·145 (3)	−0·371 (6)
H(2)	0·473 (12)	0·062 (3)	−0·529 (7)
H(3)	0·085 (12)	0·121 (3)	−0·491 (6)
H(4)	−0·508 (12)	0·202 (3)	0·328 (7)
H(5)	−0·541 (11)	0·218 (3)	0·102 (6)
H(6)	−0·148 (12)	0·228 (3)	0·255 (6)

Table 2. *Thermal parameters of non-hydrogen atoms with their standard deviations*

The β_{ij} coefficients of the expression

$$\exp\left[-(h^2\beta_{11}+k^2\beta_{22}+l^2\beta_{33}+2hk\beta_{12}+2hl\beta_{13}+2kl\beta_{23})\right]$$

are listed (× 10^4).

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
O(1)	877 (20)	24 (1)	168 (4)	14 (3)	174 (7)	3 (1)
O(2)	910 (19)	23 (1)	153 (4)	10 (3)	163 (7)	1 (1)
N(1)	706 (21)	21 (1)	151 (5)	6 (3)	118 (8)	8 (2)
N(2)	717 (21)	17 (1)	151 (4)	10 (3)	125 (8)	3 (1)
C(1)	626 (23)	20 (1)	115 (5)	1 (3)	50 (8)	2 (2)
C(2)	578 (23)	20 (1)	129 (5)	1 (3)	65 (8)	0 (2)
C(3)	577 (23)	18 (1)	119 (5)	−3 (3)	27 (8)	−2 (2)
C(4)	1080 (40)	30 (1)	166 (7)	16 (5)	194 (14)	22 (2)
C(5)	1015 (39)	21 (1)	186 (7)	31 (5)	140 (14)	−4 (2)

Discussion of the structure

The crystal structure of TMPP, projected along the a axis, is shown in Fig. 1. The ten atoms of the condensed rings lie in a plane within the limits of the experimental error. The equation of the experimental mean-square plane is

$$3{\cdot}373\,x+3{\cdot}408\,y+3{\cdot}314\,z=0\,,$$

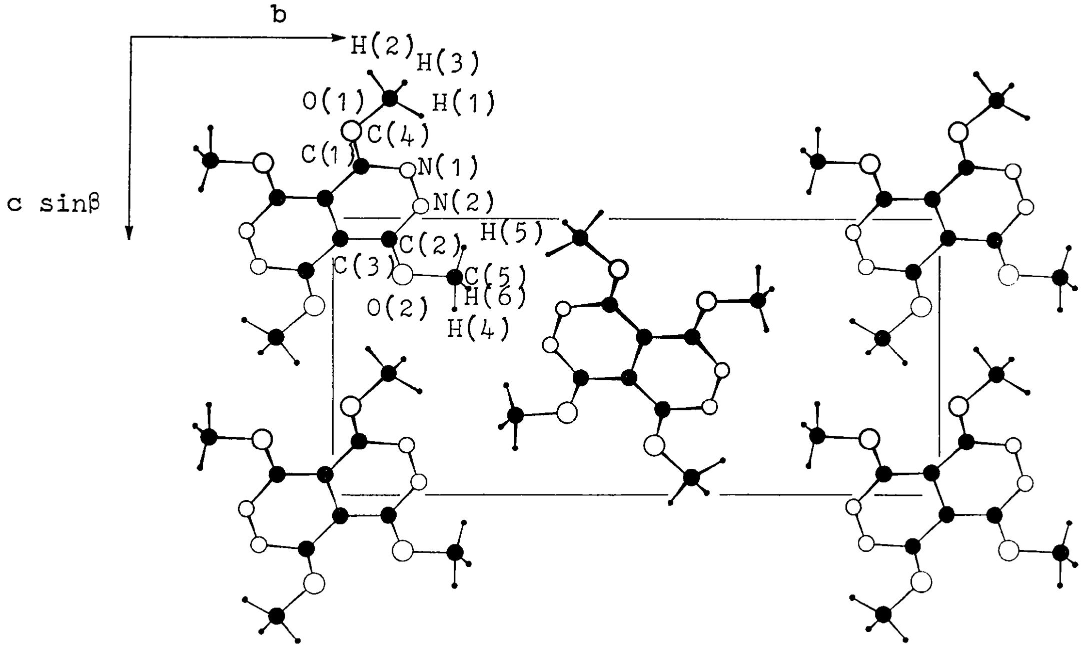

Fig. 1. Projection of the structure along the a axis.

Table 3. *Observed and calculated structure factors* (× 10)

An asterisk denotes the unobserved reflexions. *E* refers to reflexions subject to extinction.

where x, y and z are the fractional monoclinic coordinates of the atoms. Deviations from this plane are listed in Table 4. The maximum Δ for the atoms of the heterocyclic ring is 0·005Å. The oxygen atoms O(1) and O(2) of the methoxyl groups are out of the plane by 0·01 and 0·03 Å and the carbon atoms of the methyl groups are out by 0·07 and 0·11 Å. It can therefore be concluded that the whole molecule is roughly planar.

Table 4. *Deviations from the least-squares plane*

N(1)	−0·003 Å	O(1)	0·009 Å
N(2)	0·005	O(2)	−0·032
C(1)	0·001	C(4)	−0·069
C(2)	−0·005	C(5)	0·107
C(3)	0·001		

The thermal motion of TMPP molecules has been analysed as rigid-body molecular vibration on the basis of Cruickshank's (1956) procedure. The **U** tensors of the individual atoms were referred to molecular axes chosen as follows: the origin of the axes to lie at the centre of symmetry; the X axis to pass between N(1) and N(2); the Y axis to be perpendicular to X in the molecular plane; Z to be perpendicular to both X and Y axes. The

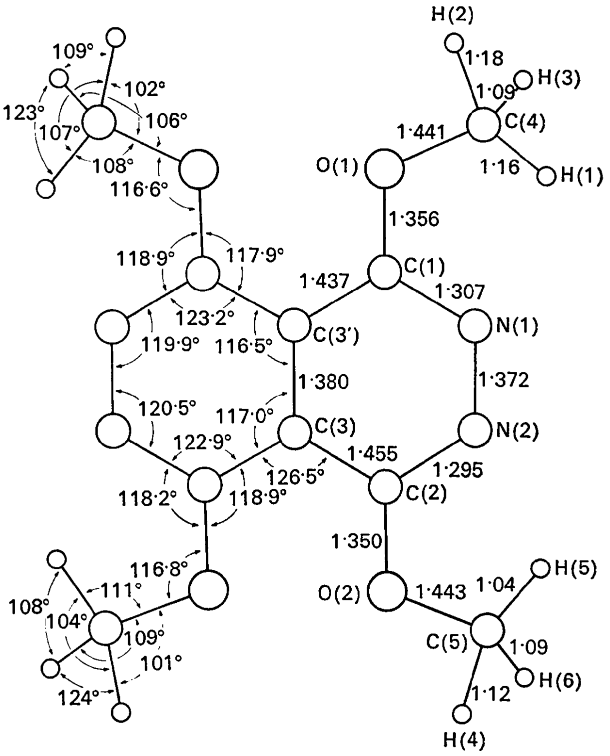

Fig. 2. Bond distances (Å) and angles in the molecule.

Table 5. *Observed and calculated components of the U tensors* (10^{-2} Å^2).

	U_{11}		U_{22}		U_{33}		U_{12}		U_{13}		U_{23}	
	obs	calc	obs	calc	obs	calc	obs	calc	obs	calc	obs	calc
O(1)	3·48	3·32	3·89	4·03	8·30	7·62	0·12	−0·21	−0·31	−0·07	0·76	0·89
O(2)	3·39	3·32	3·86	4·03	8·21	7·25	0·08	0·44	−0·38	−0·14	1·20	1·05
N(1)	2·84	2·70	4·10	4·40	6·53	6·20	−0·13	−0·04	−0·20	−0·24	0·48	0·89
N(2)	2·54	2·70	3·78	4·41	6·64	6·05	0·31	0·26	−0·34	−0·27	0·60	0·96
C(1)	2·84	2·82	4·12	4·02	4·97	5·66	0·02	−0·04	−0·06	−0·21	1·09	0·93
C(2)	2·93	2·82	3·95	4·03	4·93	5·50	0·13	0·27	−0·20	−0·24	0·64	1·01
C(3)	2·76	2·70	4·34	3·87	4·34	4·75	0·30	0·11	−0·23	−0·25	1·08	0·99
C(4)	3·47	3·65	4·82	4·50	9·97	10·32	−1·02	−0·68	0·26	0·06	1·17	0·73
C(5)	3·45	3·65	4·94	4·50	8·91	9·46	1·20	0·90	−0·02	−0·11	1·53	1·11

direction cosines of X, Y and Z referred to the crystallographic axes are

X	0·0057	0·9433	−0·3270
Y	0·6229	−0·2638	−0·8419
Z	0·7823	0·2026	0·4288

The **U** tensors calculated from rigid-body thermal motion and obtained from the structural analysis are compared in Table 5. The agreement is quite satisfactory and supports the rigid-body assumption. The traslational **T** and librational **ω** tensors are given in Table 6.

Table 6. *Translational* ***T*** (10^{-2} Å^2) *and librational* **ω** (10^{-2}rad^2) *tensors*

$$\mathbf{T} = \begin{bmatrix} 2{\cdot}66 & 0{\cdot}11 & -0{\cdot}26 \\ & 3{\cdot}87 & 0{\cdot}99 \\ & & 4{\cdot}58 \end{bmatrix}$$

$$\boldsymbol{\omega} = \begin{bmatrix} 0{\cdot}34 & -0{\cdot}02 & -0{\cdot}02 \\ & 0{\cdot}24 & 0{\cdot}01 \\ & & 0{\cdot}09 \end{bmatrix}$$

The interatomic distances and angles were corrected for rigid-body thermal libration, according to the method of Cruickshank (1961), assuming a peak shape parameter $q^2 = 0{\cdot}12$. The maximum correction in bond lengths is 4×10^{-3} Å and in bond angles is 0·2°. Therefore corrections for the angular values were neglected.

Bond distances and angles are listed in Tables 7 and 8 and sketched in Fig. 2.

Table 7. *Bond lengths with e.s.d.'s*

Distances involving non-hydrogen atoms are corrected for thermal motion

N(1)–N(2)	1·372 (4) Å	C(4)–H(1)	1·16 (5) Å
N(1)–C(1)	1·307 (4)	C(4)–H(2)	1·18 (5)
N(2)–C(2)	1·295 (4)	C(4)–H(3)	1·09 (5)
C(2)–C(3)	1·455 (4)	C(5)–H(4)	1·12 (5)
C(3)–C(3′)	1·380 (4)	C(5)–H(5)	1·04 (5)
C(1)–C(3′)	1·437 (4)	C(5)–H(6)	1·09 (5)
C(1)–O(1)	1·356 (4)		
C(2)–O(2)	1·350 (4)		
O(1)–C(4)	1·441 (4)		
O(2)–C(5)	1·443 (4)		

Table 8. *Bond angles*

N(2)–N(1)–C(1)	120·5 (2)°
N(1)–N(2)–C(2)	119·9 (2)
N(2)–C(2)–C(3)	123·2 (3)
C(2)–C(3)–C(3′)	116·5 (2)
C(3′)–C(3)–C(1′)	117·0 (2)
C(3′)–C(1)–N(1)	122·9 (3)
N(1)–C(1)–O(1)	118·2 (2)
C(1)–O(1)–C(4)	116·8 (3)
N(2)–C(2)–O(2)	118·9 (2)
C(2)–O(2)–C(5)	116·6 (3)
O(2)–C(2)–C(3)	117·9 (2)
O(1)–C(1)–C(3′)	118·9 (2)
C(2)–C(3)–C(1′)	126·5 (3)
O(1)–C(4)–H(1)	111 (2)
O(1)–C(4)–H(2)	101 (2)
O(1)–C(4)–H(3)	109 (3)
H(1)–C(4)–H(2)	104 (3)
H(1)–C(4)–H(3)	108 (3)
H(2)–C(4)–H(3)	124 (3)
O(2)–C(5)–H(4)	102 (2)
O(2)–C(5)–H(5)	108 (3)
O(2)–C(5)–H(6)	106 (3)
H(4)–C(5)–H(5)	107 (4)
H(4)–C(5)–H(6)	109 (4)
H(5)–C(5)–H(6)	123 (4)

Table 9. *Shorter intermolecular distances*

C(4)–O(1^{i})	3·49 Å	H(1)–N(2^{ii})	2·83 Å
C(4)–N(1^{i})	3·45	N(1)–H(5^{ii})	2·96
C(1)–C(2^{ii})	3·37	N(2)–H(5^{ii})	2·76
N(2)–C(5^{ii})	3·49	N(1)–H(4^{iii})	2·93
N(1)–C(5^{iii})	3·12	N(2)–H(4^{iii})	2·82
N(2)–C(5^{iii})	3·47	N(1)–H(6^{iii})	2·94
C(4)–O(2^{iv})	3·45	H(2)–O(2^{iv})	2·59
H(2)–O(1^{i})	2·34	C(4)–H(4^{iv})	2·75
H(2)–C(4^{i})	2·81	O(2)–H(3^{v})	2·68
H(1)–N(1^{ii})	2·64	H(2)–H(2^{i})	2·15

The coordinates of equivalent positions are:

Superscript			
none	x,	y,	z
(i)	$1-x$,	$-y$,	$-1-z$
(ii)	$1+x$,	y,	z
(iii)	$\frac{1}{2}+x$,	$\frac{1}{2}-y$,	$-\frac{1}{2}+z$
(iv)	$1+x$,	y,	$-1+z$
(v)	x,	y,	$1+z$

Dimensions of the heterocyclic ring are very similar to those occurring in PP. They may be explained taking into account the contribution of the 'naphthalene-like' mesomeric formulae to the molecular structure.

Bond lengths between oxygen atoms of the methoxyl groups and the carbon atoms belonging to the heterocyclic ring have a mean value of 1·353 Å, in agreement with values reported in literature for such linkages. The methyl–oxygen distances in the methoxyl groups are regular, with a mean value of 1·442 Å.

The average C–H bond length is 1·11 Å. The distance between two oxygen atoms of adjacent methoxyl groups is 2·653 Å. The shortest intermolecular contacts are listed in Table 9.

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The Crystal Structure of Devillite*

By C. Sabelli

Centro di Geochimica e Cristallochimica del Minerali del C. N. R., Istituto di Mineralogia dell'Università di Firenze, Italy

and P. F. Zanazzi

Istituto di Mineralogia dell'Università di Perugia, Italy

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Devillite, $CaCu_4(OH)_6(SO_4)_2.3H_2O$, is monoclinic, space group $P2_1/c$; with $a=20·870$, $b=6·135$, $c=22·191$ Å, $\beta=102°44'$ and $Z=8$. The crystal structure was solved by means of three-dimensional Fourier methods, starting from the atomic arrangement found for serpierite, a mineral with close analogies with devillite. The refinement by the least-squares method yielded a final R index of 0·11 for 1485 reflexions. Each copper ion, in 4+2 coordination, is linked by six edges to six adjacent copper ions forming sheets ${}^2_\infty[Cu_2(OH)_3O]^-$ parallel to (100). Two adjacent parallel sheets are connected by calcium ions in sevenfold coordination, by SO_4^{2-} tetrahedra, and by a system of hydrogen bonds. An interpretation of the complex twinning exhibited by the mineral is given. Analogies and differences with the structure of serpierite are discussed.

Introduction

Devillite is a rare hydrated basic copper calcium sulphate of formula $CaCu_4(OH)_6(SO_4)_2.3H_2O$, originally found in Cornwall (England) and first described by Pisani (1864). The mineral was later found in Hungary and studied by Březina (1879) as herrengrundite and independently by Szabo (1879), who named it urvölgyite. Meixner (1940) by comparison of chemical, optical and morphological data showed that these mineralogical species were identical.

The mineral is monoclinic; its lattice parameters were determined by Wappler (1965) who found the crystals to be one-dimensionally disordered and could not determine the space group. Faraone, Sabelli & Zanazzi (1967) re-examined the mineral and pointed out the close relationship between devillite and serpierite. The crystal structure of the latter mineral was determined by Sabelli & Zanazzi (1968). In the present study the results of a crystal structure determination on devillite are reported, and the similarities, as well as the differences, in structural features of the two minerals are explained. The structural disorder in devillite is interpreted in terms of a complex twinning.

Experimental

A sample of devillite from Herrengrund (Hungary) was used for the present work. The crystals are thin bluish-green plates flattened on {001} and striated along [010]. The lattice parameters are $a=20·870$ (2), $b=6·135$ (2), $c=22·191$ (3) Å, $\beta=102°44$ (1)$'$, as determined in a previous paper (Faraone, Sabelli & Zanazzi,

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