

The crystal-packing arrangements in the nitrate ester (I) (see Fig. 3) and alcohol (II) (Dickinson & Holden, 1979) are quite different. The latter contains a 2.27 Å O—H...O contact, and all of the remaining intermolecular distances are greater than the sums of the appropriate van der Waals radii (1.5 Å for N and 1.4 Å for O). The principal intermolecular contacts in (I) (see Fig. 3) are of the O...O type, and range from 2.96–3.07 Å. The shortest intermolecular N...O distance is 3.10 Å. That these distances are all larger than the values that would be expected on the basis of van der Waals radii of 1.5 Å for N and 1.4 Å for O is not unexpected, since the outer perimeters of the molecule bristle with NO₂'s which presumably supplement the molecule's electrostatic defenses.

The densities of (I) and (II), 2.05 and 1.95 Mg m⁻³, respectively, seem anomalously high in view of the absence of apparent close contacts that would reflect the reduction of empty space in the crystal lattices. It is concluded that the high crystal densities result from compounds which exhibit higher than normal molecular densities. The high molecular densities can be presumed to arise from having relatively compact molecules composed of sizable fractions of the denser N, O and F atoms compared to the less dense C and H atoms.

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Pyridoxine*

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Abstract. C₈H₁₁NO₃, *M_r* = 169.18, orthorhombic, space group *Pn*2₁*a*, *a* = 12.377 (2), *b* = 4.652 (1), *c* = 14.112 (2) Å, *V* = 812.54 Å³, *Z* = 4, *D_c* = 1.38, *D_o* = 1.40 Mg m⁻³, *R* = 0.048 for 724 reflections with $|F_o| > 2\sigma(F_o)$. The pyridoxine molecule occurs as the non-dipolar form in which the phenolic group remains un-ionized.

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Introduction. The crystal structure of neutral pyridoxine (PN) has been determined as part of our research on the structures and spectra of vitamin B₆ derivatives (K. J. Franklin & Richardson, 1980; T. A. Franklin & Richardson, 1980; Thompson, Balenovich, Hornich & Richardson, 1980; Longo & Richardson, 1980). The IR spectrum of PN suggested that the stable tautomer was the non-dipolar form (T. A. Franklin & Richardson, 1980). This has been confirmed by the present structure.

* 5-Hydroxy-6-methyl-3,4-pyridinedimethanol.

Colourless plate-shaped crystals of PN were grown by slow evaporation of an aqueous equimolar solution of PN.HCl and NaOH. Weissenberg photographs showed the absence of $0kl$ reflections for $k + l$ odd and of $hk0$ reflections for h odd, consistent with space groups $Pn2_1a$ or $Pnma$. A single crystal $0.22 \times 0.32 \times 0.46$ mm was aligned about the b^* axis on a manual Picker diffractometer, and cell dimensions were determined from high-angle axial reflections with Zr-filtered Mo $K\alpha$ radiation [$\lambda(\alpha_1) = 0.70926$ Å]. Data were collected by ω - 2θ scans over a 2θ range of 1.33° at a rate of 1° min^{-1} . 10 s backgrounds were counted at each end of the scan range. A standard reflection was measured after every 25–50 reflections and did not vary significantly during data collection. The reflection intensities were corrected for background and converted to structure factors by applying Lorentz and polarization corrections. No correction was made for absorption ($\mu = 0.114 \text{ mm}^{-1}$).

The structure was solved in space group $Pn2_1a$ with *MULTAN* 80 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980), and refined with the *SHELX* set of programs (Sheldrick, 1976). All atoms were located in the general positions $(x, y, z; -x, 0.5 + y, -z; 0.5 - x, 0.5 + y, 0.5 + z; 0.5 + x, y, 0.5 - z)$. Scattering factors for neutral C, H, N, and O atoms were taken from *International Tables for X-ray Crystallography* (1974). The function minimized was $\sum w\Delta^2$, where $\Delta = |F_o| - |F_c|$, $w = [\sigma^2(F_o) + 0.0004 F_o^2]^{-1}$, and $\sigma(F_o)$ is the standard deviation based on counting statistics. All non-H atoms were given anisotropic temperature factors. Positional parameters were refined for the three H atoms whose positions were not fixed geometrically [H(1), H(2), and H(3)]. The H(9), H(10) and H(11) atoms were refined as part of a rigid methyl group. The positions of the other H atoms were calculated with $r_{C-H} = 1.08$ Å. A thermal parameter was refined for the three methyl H atoms H(9)–H(11); the other H atoms were given a U of 0.06 Å².

A total of 815 reflections with $2\theta < 50^\circ$ were collected, of which 724 had $F_o > 2\sigma(F_o)$ and were classified as observed. The weighted residual, $R_w = (\sum w\Delta^2 / \sum F_o^2)^{1/2}$, was 0.046 for the observed reflections. There were no significant features on the final

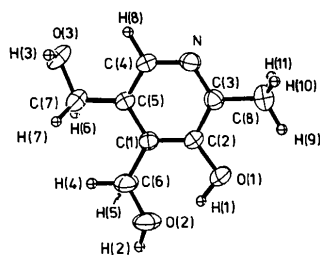


Fig. 1. Numbering scheme for pyridoxine.

difference map. The largest peaks, less than $0.25 \text{ e } \text{Å}^{-3}$, were located near the methyl group. This, coupled with the large $U(0.24 \text{ Å}^2)$ for H(9)–H(11), suggested possible disorder, but no attempt was made to refine an occupancy factor for H(9)–H(11) or to locate a second set of positions for the methyl H atoms.

The atomic positional parameters are presented in Table 1, and the numbering scheme is shown in Fig. 1. Bond distances and angles are reported in Table 2. The molecular packing is shown in Fig. 2, and the hydrogen-bonding parameters are listed in Table 3.*

* Lists of structure factors, calculated H positions and anisotropic temperature factors have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36870 (8 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Atomic parameters for pyridoxine

E.s.d.'s are given in parentheses. $U_{eq} = \frac{1}{3}(U_{11} + U_{22} + U_{33})$.

	x	y	z	U_{eq} or U_{iso} (Å ²)
N	0.3027 (2)	0.7397	0.5385 (2)	0.040 (1)
C(1)	0.2305 (3)	0.5007 (11)	0.7074 (2)	0.033 (1)
C(2)	0.3194 (3)	0.6827 (12)	0.7048 (2)	0.035 (1)
C(3)	0.3536 (3)	0.8013 (11)	0.6192 (3)	0.037 (1)
C(4)	0.2188 (3)	0.5575 (11)	0.5399 (2)	0.038 (1)
C(5)	0.1805 (3)	0.4329 (11)	0.6212 (2)	0.031 (1)
C(6)	0.1884 (4)	0.3765 (14)	0.7997 (2)	0.056 (2)
C(7)	0.0841 (3)	0.2301 (11)	0.6189 (2)	0.044 (1)
C(8)	0.4489 (3)	1.0024 (13)	0.6163 (3)	0.057 (2)
O(1)	0.3781 (2)	0.7497 (10)	0.7844 (2)	0.051 (1)
O(2)	0.2130 (3)	0.5548 (11)	0.8759 (2)	0.060 (1)
O(3)	0.0473 (2)	0.1779 (9)	0.5250 (2)	0.050 (1)
H(1)	0.336 (3)	0.684 (10)	0.837 (3)	0.06
H(2)	0.210 (3)	0.440 (10)	0.935 (3)	0.06
H(3)	0.000 (4)	0.350 (10)	0.520 (3)	0.06

Table 2. Bond distances (Å) and angles (°) for pyridoxine, with e.s.d.'s in parentheses

C(1)–C(2)	1.389 (5)	C(1)–C(6)	1.518 (5)
C(2)–C(3)	1.394 (5)	C(6)–O(2)	1.391 (5)
C(3)–N	1.332 (4)	C(2)–O(1)	1.374 (4)
N–C(4)	1.340 (5)	C(3)–C(8)	1.507 (5)
C(4)–C(5)	1.370 (5)	O(1)–H(1)	0.96 (4)
C(1)–C(5)	1.401 (4)	O(2)–H(2)	0.99 (4)
C(5)–C(7)	1.521 (5)	O(3)–H(3)	1.00 (5)
C(7)–O(3)	1.422 (4)		
C(3)–N–C(4)	119.3 (3)	C(1)–C(2)–C(3)	120.3 (3)
N–C(4)–C(5)	123.3 (3)	C(1)–C(2)–O(1)	122.3 (3)
C(4)–C(5)–C(7)	121.1 (3)	O(1)–C(2)–C(3)	117.3 (3)
C(4)–C(5)–C(1)	118.6 (3)	C(2)–C(3)–C(8)	120.5 (3)
C(1)–C(5)–C(7)	120.3 (3)	C(2)–C(3)–N	120.8 (3)
C(5)–C(7)–O(3)	112.2 (3)	N–C(3)–C(8)	118.7 (3)
C(5)–C(1)–C(6)	120.6 (3)	C(2)–O(1)–H(1)	106 (2)
C(5)–C(1)–C(2)	117.7 (3)	C(6)–O(2)–H(2)	109 (3)
C(2)–C(1)–C(6)	121.8 (3)	C(7)–O(3)–H(3)	97 (2)
C(1)–C(6)–O(2)	111.2 (3)		

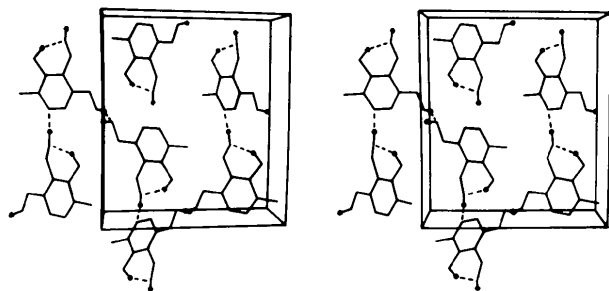


Fig. 2. Molecular packing for pyridoxine. Dotted lines indicate hydrogen bonds. H atoms involved in hydrogen bonding are shown as small spheres. The a and c axes are horizontal and vertical, respectively.

Discussion. All of the other structures so far determined of the B_6 vitamins show that the vitamin exists as a zwitterion in which the phenolic group has lost a proton and the pyridine N or amino N (if present) has gained one (Mosset, Nepveu-Juras, Haran & Bonnett, 1978; K. J. Franklin & Richardson, 1980; Longo & Richardson, 1980; Thompson *et al.*, 1980). Pyridoxine is unique in that it occurs as the non-dipolar form in the solid state. The hydroxyl and phenolic H atoms H(1)–H(3) were clearly revealed on an electron density difference map, and there was no peak near N. The C(3)–N–C(4) bond angle is 119.3° , as expected for a non-protonated pyridine ring (Singh, 1965). This angle compares favourably with the value of $119.1(3)^\circ$ observed for $\text{Cu}(\text{PM-H})_2 \cdot 2\text{H}_2\text{O}$ (K. J. Franklin & Richardson, 1980; PM-H is the pyridoxamine anion), and is significantly less than the values found for PM.HCl [$125.1(3)^\circ$; Longo & Richardson, 1980] or PN.HCl [$124.7(2)^\circ$; Bacon & Plant, 1980], both of which have protonated pyridine rings. The existence of the non-dipolar form is further supported by the C(2)–O(1) bond distance of $1.374(4) \text{ \AA}$. It is much longer than the corresponding distances in compounds having a deprotonated phenolic group [*e.g.* $1.330(3) \text{ \AA}$ in $\text{Cu}(\text{PM-H})_2 \cdot 2\text{H}_2\text{O}$, and $1.307(4)$ and $1.314(4) \text{ \AA}$ in $\text{Cu}(\text{PM})_2(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$; K. J. Franklin & Richardson, 1980], and is closer to distances observed in compounds whose phenolic groups are un-ionized [$1.343(6) \text{ \AA}$ in PN.HCl ; Bacon & Plant, 1980].

It is particularly interesting that pyridoxine does coordinate to metals as the zwitterion (Mosset *et al.*, 1978). The transformation to the zwitterion facilitates coordination by the phenolic group, and is reminiscent of the tautomeric change which occurs when pyridoxamine coordinates to metal ions (K. J. Franklin & Richardson, 1980).

There are small, but statistically significant deviations of the pyridine-ring atoms from the least-squares plane through the ring (Table 4). The non-ring atoms O(1) and C(6) are also out of the plane, on opposite sides of the ring.

The bond distances and angles other than the ones discussed above are similar to those observed in other

Table 3. *Hydrogen bonding in pyridoxine*

Symmetry superscripts: (i) $0.5 - x, 0.5 + y, 0.5 + z$; (ii) $-x, 0.5 + y, -z$.

$X-H \cdots Y$	$X \cdots Y$	$H \cdots Y$	$\angle XHY$
O(1)–H(1)–O(2)	$2.582(5) \text{ \AA}$	$1.72(4) \text{ \AA}$	$148(3)^\circ$
O(2)–H(2)–N ⁱ	$2.729(5)$	$1.74(4)$	$177(4)$
O(3)–H(3)–O(3 ⁱⁱ)	$2.697(6)$	$1.75(5)$	$158(5)$

Table 4. *Atom deviations (\AA) from the least-squares plane through the pyridine ring*

The equation of the plane is $0.6164X - 0.7761Y - 0.1331Z = -1.362$, where X, Y and Z are the coordinates in \AA . The X, Y , and Z axes are parallel to a, b , and c . Asterisks denote atoms used in the plane calculations.

C(1)*	$-0.016(4)$	C(6)	$-0.062(5)$
C(2)*	$0.010(4)$	C(7)	$0.010(4)$
C(3)*	$0.004(4)$	C(8)	$0.010(4)$
C(4)*	$0.004(4)$	O(1)	$0.066(3)$
C(5)*	$0.009(4)$		
N*	$-0.011(3)$		

structures of vitamin B_6 compounds (Bacon & Plant, 1980; K. J. Franklin & Richardson, 1980; Hanic, 1966; Longo & Richardson, 1980; Mosset *et al.*, 1978; Thompson *et al.*, 1980).

There is a fairly strong intramolecular hydrogen bond from the phenolic OH group to the adjacent CH_2OH group (Table 3), which in turn is a hydrogen-bond donor to the pyridine N atom in a glide-related molecule. The pyridoxine molecules are thus linked together in chains parallel to the $[011]$ and $[0\bar{1}1]$ directions. The chains are joined together by hydrogen bonds involving the second hydroxy group, in which each O(3) is a hydrogen-bond donor to a screw-related O(3') above and a hydrogen-bond acceptor from the screw-related O(3'') below.

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Structure of 4-Methyl-9-oxothioxanthene 10,10-Dioxide

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Abstract. $C_{14}H_{10}O_3S$, $M_r = 258.28$, orthorhombic, space group $Pnma$, $a = 14.384$ (12), $b = 6.882$ (3), $c = 11.705$ (1) Å, $V = 1158.7$ Å³, $Z = 4$, $D_c = 1.48$, $D_o = 1.48$ Mg m⁻³, $R = 0.058$ for 776 reflections with $F_o > 4\sigma(F_o)$. The thioxanthene-9-one ring is strictly planar.

Introduction. Unusual long-range coupling patterns are observed in the ¹H NMR spectra of methylthioxanthene-9-ones and their *S,S*-dioxides (Doyle, 1978). In order to try to explain this behaviour, the structures of several of these compounds are being determined. The planarity of the whole ring system is of special interest since deviations from planarity will affect the delocalization of electron density, which in turn should affect the NMR coupling constants.

Pale cream-coloured crystals were grown from warm glacial acetic acid. A single crystal 0.2 × 0.2 × 0.7 mm was mounted parallel to the needle (*b*) axis. Weissenberg photographs showed the absence of $0kl$ reflections for $k+l$ odd and of $hk0$ reflections for h odd, consistent with space groups $Pn2_1a$ or $Pnma$. The cell dimensions were determined accurately by measurement of the high-angle axial reflections with Zr-filtered Mo $K\alpha$ radiation [$\lambda(\alpha_1) = 0.70926$ Å]. Data were collected on a manual Picker diffractometer by ω - 2θ scans over a 2θ range of 2° at a rate of 2° min⁻¹. 10 s backgrounds were counted at each end of the scan range. A standard reflection was measured after every 25–50 reflections and did not vary greatly during data collection. The reflection intensities were corrected for background and converted to structure factors by applying Lorentz and polarization corrections. No correction was made for absorption ($\mu = 0.274$ mm⁻¹).

The structure was solved in space group $Pnma$ by the heavy-atom method, and subjected to full-matrix least-squares refinement with the *SHELX* set of programs (Sheldrick, 1976). The S, carbonyl O, and all

C atoms were required to lie on crystallographic mirror planes at $y = 0.25$ and 0.75 , with occupancy factors of 0.5. Scattering factors for neutral C, H, O, and S were taken from *International Tables for X-ray Crystallography* (1974). The function minimized was $\sum w\Delta^2$, where $\Delta = |F_o| - |F_c|$, $w = [\sigma^2(F_o) + 0.0049|F_o|^2]^{-1}$, and $\sigma(F_o)$ is the standard deviation based on counting statistics. All non-H atoms were given anisotropic temperature factors. The ring H-atom positions were calculated ($r_{C-H} = 1.080$ Å). One of the methyl H atoms appeared on the mirror plane on a difference map, thus fixing the orientation of the methyl group. The ring H atoms were assigned an isotropic temperature factor U of 0.08 Å²; the methyl H atoms were given $U = 0.12$ Å².

A total of 1105 unique reflections with $2\theta < 50^\circ$ were collected, of which 776 had $F_o > 4\sigma(F_o)$ and were classified as observed. The weighted residual, $R_w =$

Table 1. Atomic parameters for 4-methyl-9-oxothioxanthene 10,10-dioxide

E.s.d.'s are in parentheses. $U_{eq} = \frac{1}{3}(U_{11} + U_{22} + U_{33})$.

	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq} (Å ²)
S	0.1906 (1)	0.2500	0.3968 (1)	0.0470 (5)
O(1)	-0.1154 (3)	0.2500	0.3908 (4)	0.088 (2)
O(2)	0.2425 (2)	0.0726 (5)	0.3952 (3)	0.068 (1)
C(1)	0.1177 (4)	0.2500	0.2753 (5)	0.046 (2)
C(2)	0.1630 (5)	0.2500	0.1711 (6)	0.062 (3)
C(3)	0.1123 (6)	0.2500	0.0723 (6)	0.079 (3)
C(4)	0.0166 (6)	0.2500	0.0761 (6)	0.083 (4)
C(5)	-0.0291 (5)	0.2500	0.1795 (7)	0.069 (3)
C(6)	0.0208 (4)	0.2500	0.2824 (5)	0.047 (2)
C(7)	-0.0306 (4)	0.2500	0.3919 (6)	0.055 (2)
C(8)	0.0183 (4)	0.2500	0.5038 (5)	0.050 (2)
C(9)	-0.0367 (5)	0.2500	0.6016 (6)	0.061 (2)
C(10)	0.0039 (6)	0.2500	0.7090 (6)	0.069 (4)
C(11)	0.0996 (5)	0.2500	0.7180 (5)	0.063 (3)
C(12)	0.1565 (5)	0.2500	0.6261 (5)	0.054 (2)
C(13)	0.2619 (5)	0.2500	0.6444 (6)	0.066 (3)
C(14)	0.1164 (4)	0.2500	0.5168 (5)	0.044 (2)