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2,6-Dimethyl-3,5-diacetyl-4-(β-pyridyl)-1,4-dihydropyridine

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Abstract. $C_{16}H_{18}N_2O_2$, monoclinic, $P2_1/a$, a = 8·720 (2), b = 21·701 (3), c = 8·214 (2) Å, β = 111·81 (2)°, V = 1443 Å^3, Z = 4, D_m = 1·25, D_x = 1·24 g cm^{-3}, μ(Cu $K\alpha$) = 6·8 cm^{-1}, F(000) = 576. The structure was solved by direct methods and refined to an R of 0·044 for 1585 unique diffractometer data. The pyridyl ring plane perpendicularly bisects the 1,4-dihydropyridine ring which forms a flat boat.

Introduction. The title compound is one of the substituted dihydropyridine compounds with potential cytotoxic activity (Nantka-Namirski & Balicki, 1974). A well shaped yellow needle of the compound (approximately 0·1 × 0·15 × 0·1 mm) was used to measure the cell parameters and intensities on a CAD-4 (Enraf–Nonius) four-circle diffractometer (SLAF & BS, Kraków, Poland). Data were collected to a maximum 2θ = 120° with graphite-monochromatized Cu $K\alpha$ radiation (λ = 1·54178 Å, θ–2θ scan). Of 2182 reflections measured, 1585 were selected according to $F_o > 1{\cdot}5\sigma(F_o)$ (based on counting statistics). No correction for absorption was made.

The structure was solved by direct methods and refined by a full-matrix least-squares routine with anisotropic thermal parameters for non-hydrogen atoms and isotropic for H. The H atoms were located from a difference map. The quantity minimized was $\Sigma w(|F_o| - |F_c|)^2$, where $w = 1/\sigma^2(F_o)$. The final R value was 0·044 (R_w = 0·038).* The average shift/error value was 0·02. The X-ray atomic scattering factors used were taken from *International Tables for X-ray Crystallography* (1962). The computations were performed on a CDC 6600 (CYBER-72) computer using programs included in the XRAY 70 system (Stewart, Kundell & Baldwin, 1970) and the drawing program *ORTEP* (Johnson, 1965).

Discussion. Atomic coordinates are given in Tables 1 and 2. The interatomic distances are listed in Tables 3 and 4. Details of some least-squares planes in the molecule are given in Table 5. The bond lengths and

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32732 (3 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 1. *Fractional coordinates* (×10^4) *with e.s.d.'s in parentheses*

	x	y	z
N(1)	4965 (3)	1180 (1)	3658 (3)
C(1)	4110 (4)	650 (2)	2959 (4)
C(2)	2783 (4)	481 (1)	3364 (4)
C(3)	2214 (4)	900 (1)	4502 (4)
C(4)	3582 (4)	1339 (1)	5620 (4)
C(5)	4823 (4)	1484 (2)	5053 (4)
C(6)	699 (4)	1260 (1)	3384 (4)
C(7)	−824 (5)	1162 (2)	3522 (4)
N(2)	−2211 (3)	1461 (1)	2583 (4)
C(8)	−2130 (5)	1878 (2)	1407 (5)
C(9)	−679 (5)	2008 (2)	1160 (4)
C(10)	742 (4)	1695 (1)	2193 (4)
C(11)	2165 (6)	1401 (2)	7843 (5)
C(12)	3459 (4)	1615 (2)	7175 (4)
O(1)	4366 (3)	2039 (2)	7975 (4)
C(13)	6125 (5)	1974 (2)	5804 (5)
C(14)	4829 (5)	313 (2)	1793 (6)
C(15)	1947 (6)	−520 (2)	1407 (6)
C(16)	1760 (5)	−69 (1)	2729 (4)
O(2)	618 (4)	−157 (1)	3236 (3)

Table 2. *Refined hydrogen coordinates* (×10^3) *and thermal parameters* (Å^2) *with e.s.d.'s in parentheses*

	Bonded to	x	y	z	B_{iso}
H(1)	N(1)	575 (4)	128 (2)	329 (4)	4·4 (1·0)
H(2)	C(3)	193 (4)	64 (2)	533 (4)	3·5 (0·8)
H(3)	C(7)	−91 (4)	87 (2)	433 (4)	4·7 (1·0)
H(4)	C(8)	−333 (5)	205 (2)	49 (5)	5·3 (1·0)
H(5)	C(9)	−66 (4)	233 (2)	21 (4)	4·8 (1·0)
H(6)	C(10)	178 (4)	175 (2)	196 (4)	4·4 (0·9)
H(7)	C(11)	85 (5)	151 (2)	679 (5)	7·0 (1·1)
H(8)	C(11)	251 (5)	154 (2)	925 (5)	6·9 (1·1)
H(9)	C(11)	214 (5)	99 (2)	788 (5)	6·5 (1·1)
H(10)	C(13)	678 (5)	188 (2)	702 (5)	6·8 (1·2)
H(11)	C(13)	575 (5)	236 (2)	605 (5)	7·2 (1·2)
H(12)	C(13)	681 (5)	202 (2)	527 (5)	7·2 (1·2)
H(13)	C(14)	554 (6)	59 (2)	161 (5)	7·8 (1·2)
H(14)	C(14)	546 (5)	−7 (2)	258 (5)	7·6 (1·2)
H(15)	C(14)	403 (5)	25 (2)	59 (5)	7·4 (1·2)
H(16)	C(15)	298 (6)	−72 (2)	192 (6)	7·8 (1·2)
H(17)	C(15)	114 (6)	−81 (2)	119 (5)	7·8 (1·3)
H(18)	C(15)	176 (5)	−30 (2)	17 (6)	7·8 (1·3)

valence angles in the 1,4-dihydropyridine ring are generally close to those found in *N*-benzyl-1,4-dihydronicotinamide (Karle, 1961), except for the C=C double-bond lengths. The mean value of these (1·365 Å) is greater than that found by Karle (1·32 Å). C(3) and N(1) (Fig. 1) lie above the plane formed by C(1), C(2), C(4) and C(5), thus forming a ring with a flat-boat conformation. All methyl and acetyl substituents

Table 3. *Bond distances* (Å) *with e.s.d.'s in parentheses*

N(1)–C(1)	1·376 (4)	N(1)–H(1)	0·89 (4)
C(1)–C(14)	1·513 (6)	C(3)–H(2)	0·99 (4)
C(1)–C(2)	1·367 (6)	C(7)–H(3)	0·93 (4)
C(2)–C(16)	1·465 (4)	C(8)–H(4)	1·10 (4)
C(16)–C(15)	1·515 (6)	C(9)–H(5)	1·07 (4)
C(16)–O(2)	1·229 (6)	C(10)–H(6)	1·00 (4)
C(2)–C(3)	1·514 (5)	C(11)–H(7)	1·17 (4)
C(3)–C(4)	1·536 (4)	C(11)–H(8)	1·12 (4)
C(4)–C(12)	1·450 (5)	C(11)–H(9)	0·89 (4)
C(12)–C(11)	1·500 (7)	C(13)–H(10)	0·97 (4)
C(12)–O(1)	1·231 (4)	C(13)–H(11)	0·95 (5)
C(4)–C(5)	1·364 (6)	C(13)–H(12)	0·87 (5)
C(5)–C(13)	1·511 (5)	C(14)–H(13)	0·91 (5)
C(5)–N(1)	1·367 (5)	C(14)–H(14)	1·07 (4)
C(3)–C(6)	1·515 (4)	C(14)–H(15)	0·99 (4)
C(6)–C(7)	1·391 (6)	C(15)–H(16)	0·95 (4)
C(7)–N(2)	1·336 (4)	C(15)–H(17)	0·91 (5)
N(2)–C(8)	1·343 (5)	C(15)–H(18)	1·08 (5)
C(8)–C(9)	1·383 (6)		
C(9)–C(10)	1·391 (4)		
C(10)–C(6)	1·369 (5)		

Table 4. *Bond angles* (°) *with e.s.d.'s in parentheses*

C(1)–N(1)–C(5)	123·3 (3)	C(5)–C(4)–C(12)	122·3 (3)
N(1)–C(1)–C(14)	112·3 (3)	C(4)–C(12)–C(11)	120·5 (3)
N(1)–C(1)–C(2)	119·9 (3)	C(4)–C(12)–O(1)	122·3 (4)
C(2)–C(1)–C(14)	127·7 (3)	C(11)–C(12)–O(1)	117·2 (4)
C(1)–C(2)–C(3)	119·3 (3)	C(4)–C(5)–N(1)	120·4 (3)
C(3)–C(2)–C(16)	114·5 (3)	C(4)–C(5)–C(13)	126·5 (3)
C(1)–C(2)–C(16)	126·2 (3)	C(13)–C(5)–N(1)	113·1 (3)
C(2)–C(16)–C(15)	124·6 (4)	C(3)–C(6)–C(7)	121·0 (3)
C(2)–C(16)–O(2)	117·9 (3)	C(3)–C(6)–C(10)	122·6 (3)
O(2)–C(16)–C(15)	117·4 (3)	C(7)–C(6)–C(10)	116·3 (3)
C(2)–C(3)–C(4)	112·5 (3)	C(6)–C(7)–N(2)	124·5 (3)
C(2)–C(3)–C(6)	110·4 (2)	C(7)–N(2)–C(8)	117·6 (3)
C(4)–C(3)–C(6)	110·5 (2)	N(2)–C(8)–C(9)	122·6 (3)
C(3)–C(4)–C(5)	118·5 (3)	C(8)–C(9)–C(10)	117·8 (3)
C(3)–C(4)–C(12)	119·2 (3)	C(9)–C(10)–C(6)	121·2 (4)
H(1)–N(1)–C(1)	116 (2)	H(10)–C(13)–C(5)	110 (3)
H(1)–N(1)–C(5)	120 (2)	H(11)–C(13)–C(5)	116 (3)
H(2)–C(3)–C(2)	108 (2)	H(12)–C(13)–C(5)	115 (3)
H(2)–C(3)–C(4)	106 (2)	H(10)–C(13)–H(11)	94 (3)
H(3)–C(7)–C(6)	119 (2)	H(10)–C(13)–H(12)	107 (4)
H(3)–C(7)–N(2)	116 (2)	H(11)–C(13)–H(12)	111 (4)
H(4)–C(8)–N(2)	115 (2)	H(13)–C(14)–C(1)	105 (3)
H(4)–C(8)–C(9)	121 (2)	H(14)–C(14)–C(1)	104 (3)
H(5)–C(9)–C(10)	121 (2)	H(15)–C(14)–C(1)	113 (3)
H(5)–C(9)–C(8)	121 (2)	H(13)–C(14)–H(14)	112 (4)
H(6)–C(10)–C(6)	119 (2)	H(13)–C(14)–H(15)	101 (4)
H(6)–C(10)–C(9)	119 (2)	H(14)–C(14)–H(15)	121 (3)
H(7)–C(11)–C(12)	109 (2)	H(16)–C(15)–C(16)	108 (3)
H(8)–C(11)–C(12)	110 (2)	H(17)–C(15)–C(16)	108 (3)
H(9)–C(11)–C(12)	111 (3)	H(18)–C(15)–C(16)	112 (2)
H(7)–C(11)–H(8)	121 (3)	H(16)–C(15)–H(17)	109 (4)
H(7)–C(11)–H(9)	101 (3)	H(16)–C(15)–H(18)	114 (4)
H(8)–C(11)–H(9)	103 (3)	H(17)–C(15)–H(18)	106 (3)

Table 5. *Least-squares planes*

The equations of the planes are of the form $Px + Qy + Rz = S$, where x, y and z are in Å in orthogonal space.

Plane	Atoms defining the plane	*P*	*Q*	*R*	*S*
1	C(2), C(3), C(4)	−0·0219	0·6781	−0·7346	−1·2078
2	C(1), C(2), C(4), C(5)	0·3688	0·6224	−0·6904	−1·6535
3	N(1), C(1), C(5)	−0·5573	0·5458	−0·6257	−2·1369
4	N(2), C(7), C(9), C(10)	−0·0563	0·7124	0·6995	3·7838

Distances of atoms from the planes (Å)

Plane 2		Plane 4	
C(1)	−0·016	C(2)	0·008
C(2)	0·015	C(7)	−0·008
C(4)	−0·015	C(9)	−0·007
C(5)	0·016	C(10)	0·008
N(1)	0·137	C(6)	−0·006
C(3)	0·295	C(8)	−0·003
C(13)	−0·047		
C(14)	−0·233		
C(12)	−0·250		
C(16)	−0·136		
O(1)	−0·297		
O(2)	−0·095		

Angles between the planes

1–2	159·6°	2–3	167·7°	2–4	89·9°

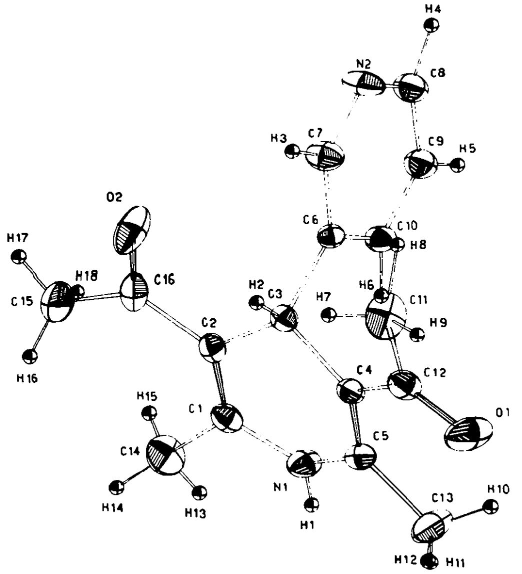

Fig. 1. An *ORTEP* diagram of the molecule.

Table 6. *Intermolecular distances less than* 3·5 Å

O(1)–C(8^{i})	3·317 (4)	C(14)–N(2^{ii})	3·471 (7)
N(1)–N(2^{ii})	2·972 (4)	O(2)–C(9^{iii})	3·396 (5)
H(1)–N(2^{ii})	2·11 (4)	C(6)–O(1^{iv})	3·347 (5)

Symmetry code

(i) $1+x,\ y,\ 1+z$ (iii) $-x,\ -y,\ 1-z$
(ii) $1+x,\ y,\ z$ (iv) $-\frac{1}{2}+x,\ \frac{1}{2}-y,\ -1+z$

are slightly below this plane. Both acetyl groups are directed counter to one another showing that there is no symmetry element in the molecule. Practically the same C=O bond lengths are observed for both carbonyl groups. The β-pyridyl ring is attached to C(3) in a pseudo-axial position and lies in a plane perpendicular to the mean plane of the 1,4-dihydropyridine ring. The calculation of the intermolecular distances (Table 6) reveals the possible existence of a hydrogen bond between the N(1) and N(2^{ii}) atoms belonging to neighbouring molecules: H(1)···N(2^{ii}) is 2·11 (4) Å and N(1)–H(1)···N(2^{ii}) is 175 (3)°. In this way the molecules form parallel straight chains along the x axis of the asymmetric unit, the bonded molecules having the same symmetry operation with an x translation.

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Copper(II) Phosphate

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Abstract. Triclinic, $P\bar{1}$, $a = 4{\cdot}8537$ (7), $b = 5{\cdot}2855$ (6), $c = 6{\cdot}1821$ (8) Å, $\alpha = 72{\cdot}35$ (1), $\beta = 86{\cdot}99$ (1), $\gamma = 68{\cdot}54$ (1)°, $Cu_3(PO_4)_2$, $Z = 1$, $D_x = 4{\cdot}503$ g cm^{-3}, isostructural with stranskiite. Crystals were grown hydrothermally from 0·1 M H_3PO_4 at 450 °C at 40 000 p.s.i.

Introduction. As part of a continuing study of the crystal chemistry of basic phosphates of the divalent Cu ion (Anderson, Shoemaker, Kostiner & Ruszala, 1977; Shoemaker, Anderson & Kostiner, 1977) we have grown single crystals of anhydrous $Cu_3(PO_4)_2$ and determined its crystal structure.

Hanawalt, Rinn & Frevel (1938) reported the X-ray powder diffraction pattern of a 'fused salt', $Cu_3(PO_4)_2$, which was positively identified by Royen & Brenneis (1963). Although $Cu_3(PO_4)_2$ often appears in the literature as the assumed precipitation product of low-temperature neutralization reactions, these reactions generally result in a highly hydrated amorphous mixture or a crystalline hydroxyphosphate [*e.g.* libethenite, $Cu_2(PO_4)OH$]. Crystals of $Cu_3(PO_4)_2$ of a size suitable for single-crystal X-ray diffraction have apparently not been produced and identified until this time.

A blue powder containing predominantly $Cu_3(PO_4)_2$ was produced by repeated sintering of $(NH_4)_2HPO_4$ and CuO at 1000 °C for 5 d. This powder was welded into a gold capsule with 0·1 M H_3PO_4 solution in the ratio of 0·1 g powder to 0·4 ml solution, placed into a cold-seal hydrothermal bomb and heated under hydrostatic pressure to 450 °C. Crystals of $Cu_3(PO_4)_2$ up to 0·4 mm in size have been produced after 5 d at 32 000–45 000 p.s.i.

Precession photographs revealed triclinic symmetry. Subsequent analysis showed the space group to be $P\bar{1}$, in which the final refinements were carried out.

Attempts to grind a crystal into a spherical shape were foiled by a well-developed cleavage. Data were therefore collected on a small euhedral crystal with dimensions 0·11 × 0·08 × 0·08 mm ($V = 0{\cdot}97 \times 10^{-3}$ cm^3). Three pairs of well-developed faces were found to