

1,2-Dihydro-*N*-(2-hydroxyethyl)-4,6-dimethyl-2-oxopyrimidine

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(Received 16 November 1990; accepted 6 December 1991)

Abstract. $C_8H_{12}N_2O_2$, $M_r = 169.2$, monoclinic, $P2_1$, $a = 5.082$ (1), $b = 11.719$ (1), $c = 7.224$ (1) Å, $\beta = 107.97$ (5)°, $V = 409.2$ (3) Å³, $Z = 2$, $D_x = 1.37$ Mg m⁻³, $\lambda(\text{Mo } K\alpha) = 0.71073$ Å, $\mu = 0.093$ mm⁻¹, $F(000) = 180$, room temperature, $R = 0.054$, $wR = 0.066$ for 1030 reflections ($F^2 > 3\sigma$) out of 1544 measurements. The pyrimidine ring is planar within 0.009 (3) Å, and almost perpendicular to the adjacent C—C bond [torsion angle C(2)—N(1)—C(7)—C(8) = -74.4 (4)°]. The N—C—C—O moiety has the *sc* conformation [torsion angle -61.4 (4)°]. The molecules do not form dimers, but infinite zigzag chains along the *b* axis through hydrogen bonds OH...N(3'). Since it is not an acceptor to an H bond, the C(2)=O(2) length is 1.225 (5) Å.

Introduction. As part of a series of studies on the elementary binding patterns in protein–nucleic acid interactions the crystal structures of three *N*-(2-hydroxyethyl)pyrimidine derivatives have been reported (Shibata, Takenaka, Sasada & Ohki, 1985*a,b*; Shibata, Takenaka & Sasada, 1985). Each compound showed a different H-bonding scheme, the rationalization of which is complicated because of the large number of possible H donors and acceptors, as well as by the possible influence of tautomeric forms. To continue the investigation into the patterns of H bonding between a hydroxyl group and a pyrimidine ring we have determined the structure of the title compound (1). The compound (see Fig. 1 for atomic numbering) has only one H donor, two possible acceptors [O(2) and N(3)] and no tautomeric forms.

Experimental. (1) was synthesized according to Reznik & Pashkurov (1966). Single crystal (m.p. 412–413 K) obtained by slow evaporation from acetonitrile. Enraf–Nonius CAD-4 diffractometer, graphite-monochromated Mo $K\alpha$ radiation, colourless needle-like crystal (0.2 × 0.1 × 0.1 mm), unit-cell dimensions from 25 high-angle reflections, intensities between $4 < 2\theta < 50^\circ$, $-6 < h < 6$, $-13 <$

$k < 13$, $0 < l < 8$; $\omega/(\frac{5}{3}\theta)$ scan mode; scan width $\omega = (1.35 + 0.35\text{tg}\theta)^\circ$, two orientation-control reflections and two intensity-control reflections every 200 measurements showing no angular deviations but 7% intensity drop, linear correction of intensity was applied; corrections for Lorentz and polarization factors, but not for absorption or extinction; 1544 reflections measured, 1030 with $I > 3\sigma(I)$. Structure solved using *MULTAN* (Germain, Main & Woolfson, 1971), all H atoms found in difference electron density maps. Full-matrix least-squares refinements (on F^2 's) of all positional parameters, non-H atoms refined anisotropically, H atoms isotropically with fixed B_{iso} ; $\sum w(|F_o| - |F_c|)^2$ minimized with $w = 4|F_o|^2 / \{[\sigma(I)^2] + [0.07|F|^2]\}$, convergence reached at $R = 0.054$, $wR = 0.066$, $S = 2.3$, $(\Delta/\sigma)_{\text{max}} = 0.03$, 145 variables using 1030 reflections with $F_o^2 > 3\sigma$. No assignment of absolute structure made. Maximum of $0.5 \text{ e } \text{Å}^{-3}$ in final difference Fourier synthesis. Atomic scattering functions from *International Tables for X-ray Crystallography* (1974, Vol. IV). Enraf–Nonius *SDP* (Frenz, 1978) employed. Refined parameters* are given in Table 1, atomic numbering scheme in Fig. 1.

Discussion. Bond distances and valence angles are given in Table 2, torsion angles defining some conformational details in Fig. 2. Four intramolecular phenomena attract attention. First, comparing the data with those obtained for *N*-(2-hydroxyethyl)-cytosine (2), *N*-(2-hydroxyethyl)thymine monohydrate (3) and *N*-(2-hydroxyethyl)uracil (4) (Shibata, Takenaka, Sasada & Ohki, 1985*a,b*; Shibata, Takenaka & Sasada, 1985) one notes considerable differences between (1) on the one hand and (3) and (4) on the other, whereas the differences

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54943 (14 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Fractional atomic coordinates and isotropic temperature parameters (\AA^2)

The e.s.d.'s given in parentheses refer to the last significant digit. Isotropic temperature parameters are calculated from anisotropic temperature parameters using

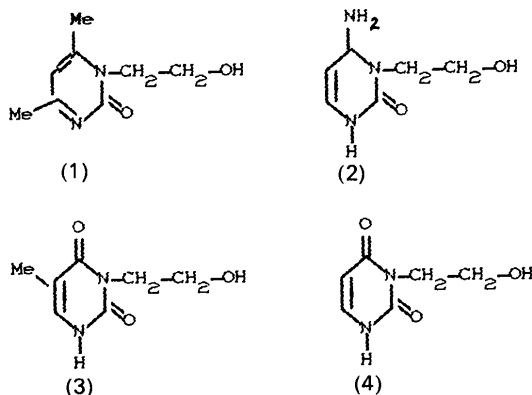
$$B_{\text{eq}} = (4/3)[a^2 B(1,1) + b^2 B(2,2) + c^2 B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)].$$

All anisotropic temperature parameters were physically acceptable. H(*i,j*) is *j*th H atom attached to atom *i*.

	<i>x</i>	<i>y</i>	<i>z</i>	B_{eq}
O(1)	0.2907 (6)	0.3926 (2)	1.0082 (5)	4.47 (7)
O(2)	0.2384 (6)	0.0665 (2)	1.1520 (4)	4.13 (6)
N(1)	0.4261 (6)	0.163*	0.9499 (4)	2.40 (6)
N(3)	0.0850 (6)	0.0191 (2)	0.8323 (4)	2.91 (6)
C(2)	0.2475 (7)	0.0797 (3)	0.9859 (5)	2.70 (7)
C(4)	0.1047 (7)	0.0362 (3)	0.6580 (5)	2.65 (7)
C(5)	0.2860 (8)	0.1165 (3)	0.6211 (5)	3.09 (8)
C(6)	0.4465 (7)	0.1801 (3)	0.7685 (5)	2.60 (7)
C(7)	0.5807 (8)	0.2333 (4)	1.1188 (5)	3.07 (8)
C(8)	0.3961 (8)	0.3193 (3)	1.1683 (6)	3.36 (8)
C(9)	-0.0814 (9)	-0.0330 (4)	0.4948 (7)	3.87 (9)
C(10)	0.6417 (8)	0.2679 (3)	0.7383 (6)	3.75 (9)
H(0,1)	0.16 (1)	0.437 (4)	1.020 (8)	4.0
H(5,1)	0.29 (1)	0.125 (4)	0.482 (7)	4.0
H(7,1)	0.648 (9)	0.180 (5)	1.227 (6)	4.0
H(7,2)	0.74 (1)	0.259 (4)	1.081 (7)	4.0
H(8,1)	0.23 (1)	0.282 (5)	1.209 (8)	4.3
H(8,2)	0.53 (1)	0.367 (5)	1.286 (7)	4.3
H(9,1)	-0.07 (1)	-0.125 (5)	0.523 (7)	4.0
H(9,2)	-0.039 (9)	-0.019 (4)	0.370 (7)	4.0
H(9,3)	-0.264 (9)	0.001 (5)	0.475 (8)	4.7
H(10,1)	0.64 (1)	0.263 (4)	0.598 (7)	4.0
H(10,2)	0.84 (1)	0.252 (4)	0.822 (8)	4.6
H(10,3)	0.61 (1)	0.343 (4)	0.778 (7)	4.6

* Origin-fixing parameter.

between (1) and (2) are smaller. These differences are most pronounced in the bond lengths and angles near N(3), C(4) and C(5). This reflects the fact that (1) has only the structure shown in Fig. 1, while in the other compounds tautomeric forms play a role. For example, the N(3)—C(4) bond has the most double-bond character in (1), slightly less in (2) and much less in (3) and (4). Consequently, the N(3)—C(4) length increases in the sequence (1) < (2) ≪ (3) < (4).

Table 2. Geometry of the title compound: distances in \AA angles in $^\circ$, with e.s.d.'s in parentheses

N(1)—C(2)	1.408 (4)	C(2)—O(2)	1.225 (5)
C(2)—N(3)	1.361 (4)	C(4)—C(9)	1.501 (5)
N(3)—C(4)	1.309 (6)	C(6)—C(10)	1.490 (6)
C(4)—C(5)	1.399 (5)	N(1)—C(7)	1.483 (5)
C(5)—C(6)	1.349 (5)	C(7)—C(8)	1.493 (6)
C(6)—N(1)	1.362 (5)	C(8)—O(1)	1.407 (5)
C(2)—N(1)—C(6)	121.8 (2)	N(3)—C(4)—C(9)	117.1 (3)
C(2)—N(1)—C(7)	116.2 (3)	C(5)—C(4)—C(9)	120.5 (3)
C(6)—N(1)—C(7)	122.1 (3)	C(4)—C(5)—C(6)	119.7 (4)
N(1)—C(2)—N(3)	118.3 (3)	C(5)—C(6)—N(1)	118.0 (3)
N(1)—C(2)—O(2)	119.3 (3)	C(5)—C(6)—C(10)	122.3 (4)
N(3)—C(2)—O(2)	122.4 (4)	N(1)—C(6)—C(10)	119.7 (3)
C(2)—N(3)—C(4)	119.8 (3)	N(1)—C(7)—C(8)	111.1 (3)
N(3)—C(4)—C(5)	122.5 (3)	C(7)—C(8)—O(1)	108.9 (3)

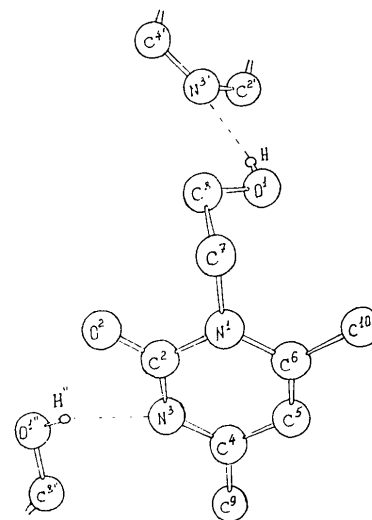


Fig. 1. Atomic numbering scheme of the title compound and the H bond in the crystal.

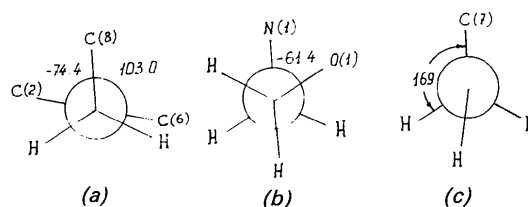


Fig. 2. Newman projections in (1) showing the conformation along (a) N(1)—C(7), (b) C(7)—C(8) and (c) C(8)—O(1).

Second, the pyrimidine ring is planar within the limits of error with C(2) deviating most [0.009 (3) \AA]. Most substituents, however, are not in the plane: O(2) -0.017 (3), C(7) 0.108 (4), C(9) 0.035 (5), C(10) 0.009 (4) \AA .

Third, the pyrimidine ring and the C(7)—C(8) bond are almost perpendicular to one another. This is a feature common to all pyrimidine compounds mentioned [(1)–(4)] and to other compounds possessing the C—C—OH moiety attached to an aromatic

ring. It also occurs in ethylbenzene and its derivatives (Kataeva, Litvinov, Strobykina & Kataev, 1990; Scharfenberg, Roszondai & Hargittai, 1980).

Fourth, the N(1)—C(7)—C(8)—O(1) moiety has the *sc* conformation with C(8)—O(1) pointing towards the C(6) side of the pyrimidine ring. The *sc* conformation seems the usual form for the moiety irrespective of whether the trigonal N is part of a ring or not (Kataev, 1990). In this respect the N—C—C—OH moiety in (1)–(4) follows the conformational behaviour of 2-aminoethanol in which heavy-atom *gauche* forms are favoured over heavy-atom *trans* forms (Van Alsenoy, Stam, Ewbank & Schafer, 1986).

We now turn to the H-bonding scheme and note that the molecules in (1) form infinite zigzag chains along the *b* axis, O(1)—H \cdots N(3')(-*x*, $\frac{1}{2} + y$, 2 - *z*) with the following parameters: O(1)—H 0.88 (5), H \cdots N(3') 2.11 (5), O(1) \cdots N(3') 2.920 (5) Å, O(1)—H \cdots N(3') 156 (1)°. In contrast, compounds (2)–(4) all primarily form dimers instead of polymers. One consequence of the O(1)—H \cdots N(3') bridge in (1) is that O(2) is not an acceptor to an H bond. Thus, the C(2)=O(2) bond length is 1.225 (5) Å, very close to the value expected (1.225 Å) for a free, unbridged C=O bond (Popelier, Lenstra, Van Alsenoy & Geise, 1990). In the related compound (2), C(2)=O(2) is engaged in H bonding and the bond is indeed lengthened [1.246 (2) Å]. Another consequence is the value $\varphi = 169$ (3)° for the torsion angle C(7)—C(8)—O(1)—H. We also calculated this angle for compounds (2)–(4) using the data retrieval system of the Cambridge Structural Database (Allen *et al.*, 1979), and found -111 (2)° in (2), 93 (2)° in (3) and 78 (3)° in (4). The scatter means that the conformation of

the C(7)—C(8)—O(1)—H moiety is dictated by the H-bonding scheme adopted by the particular compound.

This research has been performed as part of project I.6 within the framework of the scientific and technological cooperation between the Belgium–Luxembourg Economic Union and the USSR.

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Acta Cryst. (1992). C48, 1288–1290

Structure of Difluorotriphenylphosphorane

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(Received 25 July 1991; accepted 17 December 1991)

Abstract. C₁₈H₁₅F₂P, *M_r* = 300.29, orthorhombic, *Pbcn*, *a* = 6.105 (2), *b* = 16.634 (3), *c* = 14.356 (3) Å, *V* = 1458 (1) Å³, *Z* = 4, *D_x* = 1.368 Mg m⁻³, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu = 0.194$ mm⁻¹, *F*(000) = 624, *T* = 294 K, *R* = 0.045 for 729 observed independent reflections. Difluorotriphenylphosphorane [(C₆H₅)₃PF₂] displays a trigonal bipyramidal geometry about the P atom, with the two F atoms

occupying axial positions. The three phenyl groups in the equatorial positions are not 'geared' in a regular propeller arrangement; one of the three rings is twisted in the opposite direction to that of the other two.

Introduction. Fluorophosphoranes have featured prominently in studies of pentavalent phosphorus