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2,3-Dihydro-6-hydroxy-1,3-dimethyl-7-propyl-9-(2-thienylmethyl)pyrimido[2,1-*f*]purine-4,8(1*H*,9*H*)-dione

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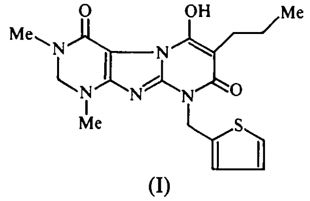
(*Received* 15 *April* 1993; *accepted* 18 *October* 1993)

Abstract

The molecular structure of $C_{18}H_{21}N_5O_3S$ comprises an almost planar purine ring fused to a reduced pyrimidine ring. An intramolecular O···O distance of 2.492 (3) Å indicates the presence of hydrogen bonding.

Comment

The present compound (I) belongs to a series of substituted 2,3-dihydro-6-hydroxypyrimido[2,1-*f*]-purine-4,8(1*H*,9*H*)-diones having anti-inflammatory activity in the adjuvant-induced arthritis rat model. Crystal structure analysis has been carried out to show the effect of substituents on the molecular geometry and conformation.



(I)

The almost planar purine ring is fused to the reduced pyrimidine ring with dihedral angles of 4.4 (1) (between planes *A* and *B*) and 3.6 (1)° (between planes *B* and *C*). Only atom C2 of the reduced pyrimidine ring *A* deviates significantly from the best plane of the remaining ring atoms. The lengthening of the bond O13—C4 [1.265 (5) Å] from the normal C=O distance may be a result of the intramolecular O14···O13 hydrogen bonding. Atom C9 is bonded to three N atoms. The bond lengths indicate a double bond to N10 [1.313 (4) Å] and single bonds to N5 [1.394 (5) Å] and N9 [1.346 (3) Å]. The endocyclic angle around N9 is greater than those around N1 and N3. All these structural features are comparable to those in 2,2-dimethyl-1,2,3,4-tetrahydrobenzimidazo[3,2-*a*]pyrimid-4-one (Bird, Nyburg & Parkins, 1991). The conformation of the side chain relative to the fused ring system is described by the torsion angles about the bonds C7—C15 and C15—C16. The thiophene ring geometry is comparable to that found in 4-(4,6-dimethyl-2-pyridyl)-2-thiophene carboxamide (Rodier, Robert & Le Baut, 1992). The dihedral angle between the fused ring plane and the thiophene ring plane is 115.5 (2)°.

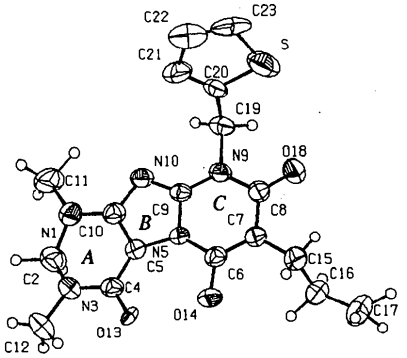


Fig. 1. A view of the molecule with 50% probability anisotropic displacement ellipsoids for the non-H atoms and atomic numbering scheme.

Experimental

The compound was synthesized and supplied by Dr James Kaminski, Pharmaceutical Research Division, New Jersey, USA. Crystals were obtained by slow evaporation from chloroform/methanol (1:1) solution.

Crystal data

$C_{18}H_{21}N_5O_3S$
$M_r = 387.4$
Monoclinic
$P2_1/a$
$a = 11.426$ (1) Å
$b = 16.090$ (1) Å
$c = 11.359$ (1) Å
$\beta = 118.37$ (1)°
$V = 1837.5$ (3) Å^3
$Z = 4$

$D_x = 1.401$ Mg m^{-3}
Cu $K\alpha$ radiation
$\lambda = 1.5418$ Å
Cell parameters from 25 reflections
$\theta = 58\text{-}61°$
$\mu = 1.77$ mm^{-1}
$T = 296$ K
Plate
0.9 × 0.7 × 0.3 mm
Colourless

Data collection

Rigaku AFC-6*S* diffractometer
$\omega/2\theta$ scans
3105 measured reflections
2707 independent reflections
2497 observed reflections
  $[F > 3\sigma(F)]$
$\theta_{\max} = 60°$
$h = -13 \rightarrow 13$
$k = 0 \rightarrow 18$
$l = 0 \rightarrow 13$
2 standard reflections
  monitored every 50 reflections
  intensity variation: <1.0%

Refinement

Refinement on *F*
$R = 0.068$
$wR = 0.068$
$S = 1.03$
2497 reflections
332 parameters
Unit weights applied
$(\Delta/\sigma)_{\max} < 0.3$
$\Delta\rho_{\max} = 0.43$ e Å^{-3}
$\Delta\rho_{\min} = -0.27$ e Å^{-3}
Extinction correction: none
Atomic scattering factors
  from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$$U_{\rm eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
C20	−0.0644 (5)	0.1792 (4)	0.1241 (5)	0.052 (2)
C21	−0.0781 (6)	0.1458 (5)	0.0073 (7)	0.074 (4)
C22	0.0441 (9)	0.1029 (5)	0.0340 (11)	0.098 (5)
C23	0.1399 (8)	0.1093 (5)	0.1607 (10)	0.093 (5)
S	0.0865 (2)	0.1547 (1)	0.2652 (2)	0.089 (1)
C20′	−0.0524 (9)	0.1840 (5)	0.1509 (8)	0.023 (4)
C21′	0.0654 (14)	0.1551 (10)	0.2520 (13)	0.067 (5)
C22′	0.1329 (16)	0.1042 (9)	0.1920 (23)	0.083 (12)
C23′	0.0738 (18)	0.1033 (10)	0.0664 (25)	0.093 (14)
S′	−0.0822 (5)	0.1409 (3)	−0.0023 (5)	0.086 (3)
N1	−0.6239 (3)	0.1702 (2)	−0.2792 (3)	0.057 (11)
C2	−0.7654 (4)	0.1605 (3)	−0.3172 (5)	0.065 (2)
N3	−0.7859 (3)	0.0882 (2)	−0.2529 (3)	0.053 (1)
C4	−0.7068 (3)	0.0737 (2)	−0.1235 (3)	0.043 (1)
C5	−0.5869 (3)	0.1212 (2)	−0.0687 (3)	0.042 (1)
N5	−0.4767 (3)	0.1193 (2)	0.0600 (3)	0.039 (1)
C6	−0.4570 (3)	0.0875 (2)	0.1792 (3)	0.042 (1)
C7	−0.3415 (3)	0.1001 (2)	0.2924 (3)	0.045 (1)
C8	−0.2383 (3)	0.1515 (2)	0.2850 (3)	0.048 (1)
N9	−0.2653 (3)	0.1797 (2)	0.1602 (3)	0.043 (1)
C9	−0.3799 (3)	0.1655 (2)	0.0475 (3)	0.039 (1)
N10	−0.4165 (3)	0.1901 (2)	−0.0753 (3)	0.044 (1)
C10	−0.5453 (3)	0.1629 (2)	−0.1473 (3)	0.044 (1)
C11	−0.5958 (6)	0.2302 (5)	−0.3587 (7)	0.095 (3)
C12	−0.9183 (4)	0.0485 (4)	−0.3218 (6)	0.073 (2)
O13	−0.7335 (2)	0.0206 (2)	−0.0576 (3)	0.054 (1)
O14	−0.5560 (2)	0.0422 (2)	0.1773 (3)	0.054 (1)
C15	−0.3173 (4)	0.0651 (3)	0.4231 (4)	0.055 (2)
C16	−0.3812 (5)	0.1124 (3)	0.4930 (4)	0.059 (2)
C17	−0.3430 (7)	0.0783 (5)	0.6298 (6)	0.087 (3)
O18	−0.1317 (3)	0.1678 (2)	0.3842 (3)	0.064 (1)
C19	−0.1639 (4)	0.2326 (2)	0.1477 (4)	0.050 (2)

Table 2. *Selected geometric parameters* (Å, °)

C20—C21	1.370 (10)	N5—C6	1.362 (5)
C20—S	1.752 (5)	N5—C9	1.394 (5)
C20—C19	1.547 (8)	C6—C7	1.350 (3)
C21—C22	1.454 (12)	C6—O14	1.337 (5)
C22—C23	1.335 (12)	C7—C8	1.475 (5)
C23—S	1.733 (12)	C7—C15	1.486 (6)
C20′—C21′	1.370 (14)	C8—N9	1.377 (5)
C20′—S′	1.750 (11)	C8—O18	1.232 (4)
C21′—C22′	1.493 (30)	N9—C9	1.346 (3)
C22′—C23′	1.255 (34)	N9—C19	1.498 (6)
C23′—S′	1.682 (19)	C9—N10	1.313 (4)
N1—C2	1.470 (6)	N10—C10	1.372 (4)
N1—C10	1.337 (4)	C15—C16	1.514 (8)
N1—C11	1.458 (9)	C16—C17	1.504 (8)
C2—N3	1.451 (6)	O14···O13	2.493 (3)
N3—C4	1.330 (4)	N3···C7$^{\rm i}$	3.481 (5)
N3—C12	1.478 (5)	C4···C6$^{\rm i}$	3.429 (5)
C4—C5	1.428 (4)	N5···O13$^{\rm i}$	3.301 (5)
C4—O13	1.265 (5)	N9···O13$^{\rm i}$	3.425 (5)
C5—N5	1.405 (4)	C9···O13$^{\rm i}$	3.243 (5)
C5—C10	1.370 (5)		
S—C20—C19	116.8 (3)	C5—N5—C9	104.1 (3)
C21—C20—C19	129.1 (5)	C5—N5—C6	133.3 (3)
C21—C20—S	114.0 (5)	C6—N5—C9	122.5 (3)
C20—C21—C22	109.1 (6)	N5—C6—O14	116.7 (3)
C21—C22—C23	113.7 (9)	N5—C6—C7	121.0 (3)
C22—C23—S	113.3 (8)	C7—C6—O14	122.2 (3)
C20—S—C23	89.0 (4)	C6—C7—C15	121.9 (3)
C21′—C20′—S′	110.4 (9)	C6—C7—C8	118.4 (3)
C20′—C21′—C22′	108.6 (12)	C8—C7—C15	119.7 (3)
C21′—C22′—C23′	114.2 (16)	C7—C8—O18	122.5 (3)
C22′—C23′—S′	113.7 (19)	C7—C8—N9	116.7 (3)
C20′—S′—C23′	91.1 (7)	N9—C8—O18	120.8 (3)
C10—N1—C11	121.6 (4)	C8—N9—C19	118.7 (3)
C2—N1—C11	115.1 (4)	C8—N9—C9	124.3 (3)
C2—N1—C10	112.3 (3)	C9—N9—C19	116.9 (3)
N1—C2—N3	110.8 (4)	N5—C9—N9	117.9 (3)
C2—N3—C12	116.7 (4)	N9—C9—N10	129.3 (3)
C2—N3—C4	120.6 (3)	N5—C9—N10	113.7 (3)
C4—N3—C12	119.8 (3)	C9—N10—C10	104.3 (3)
N3—C4—O13	123.0 (3)	C5—C10—N10	111.9 (3)
N3—C4—C5	113.3 (3)	N1—C10—N10	126.8 (3)
C5—C4—O13	123.7 (3)	N1—C10—C5	121.1 (3)
C4—C5—C10	122.4 (3)	C7—C15—C16	115.2 (4)
C4—C5—N5	129.9 (3)	C15—C16—C17	112.5 (5)
N5—C5—C10	105.8 (3)	C20—C19—N9	111.5 (3)
C6—C7—C15—C16	−79.0 (5)	C9—N9—C19—C20	−92.6 (4)
C8—C7—C15—C16	99.9 (4)	N9—C19—C20—C21	82.1 (7)
C7—C15—C16—C17	−174.9 (4)	N9—C19—C20—S	−96.2 (4)
C8—N9—C19—C20	89.7 (4)		

Symmetry code: (i) $-1-x, -y, -z$.

Isotropic least-squares refinement converged to $R = 0.172$. The thiophene ring appeared to be disordered and was refined in two positions: the occupancy factors were found to be $p = 0.70$ for one orientation and $1-p$ for the other. The thiophene ring with $p = 0.30$ was refined isotropically. Out of 21 H atoms, 17 were located on the difference Fourier map and refined isotropically. Program(s) used to solve structure: *MULTAN*78 (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978). Program(s) used to refine structure: *SHELX*76 (Sheldrick, 1976). Molecular graphics: *ORTEP*II (Johnson, 1976). Software used to prepare material for publication: *PARST* (Nardelli, 1983).

Lists of structure factors, anisotropic displacement parameters and H-atom coordinates have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71760 (14 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: HA1059]

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Acta Cryst. (1994). C**50**, 954–955

A (2*R*,5*S*)-2-*o*-Anisyl-3-oxa-1-aza-2-phosphabicyclo[3.3.0]octane–Borane Complex

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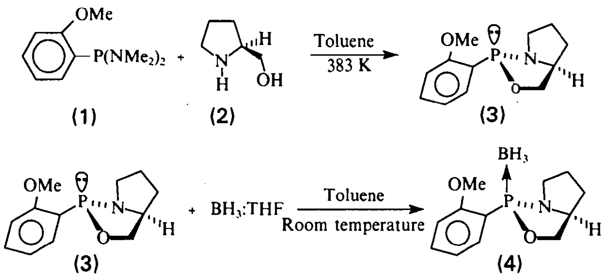
(*Received* 7 *June* 1993; *accepted* 21 *October* 1993)

Abstract

(2*R*,5*S*)-2-(2-Methoxyphenyl)-3-oxa-1-aza-2-phosphabicyclo[3.3.0]octane(*P*—*B*)borane, $C_{12}H_{19}BNO_2P$, is one of a series of new chiral oxazaphospholidine–borane complexes used as catalysts in the enantioselective borane reduction of ketones. The structure and the absolute configuration about the P atom were determined.

Comment

Recently, we reported a new method for the enantioselective reduction of ketones with BH_3:THF catalyzed by a chiral tricoordinated phosphorus–borane complex (4) (Brunel, Pardigan, Faure & Buono, 1992). Complex (4) was synthesized by the reaction of bis(dimethylamino)-*o*-anisylphosphine (1) with (*S*)-(+)-prolinol (2) in refluxing toluene and complexation by one equivalent of BH_3:THF.



The study of the title compound (4) was undertaken in order to probe the mechanism of the reduction and to establish the absolute configuration about the P atom. The structure is shown in Fig. 1. It is noteworthy that the sum of the bond angles around the N atom is 341.6°, showing that the configuration is non-planar. Nevertheless, the short P—N bond [1.661 (3) Å] involves a $p\pi$–$d\pi$ contribution but does not exclude complexation to another molecule of borane, as observed by ^{31}P and ^{11}B NMR spectroscopy (Buono, Brunel, Faure & Pardigon, 1993).

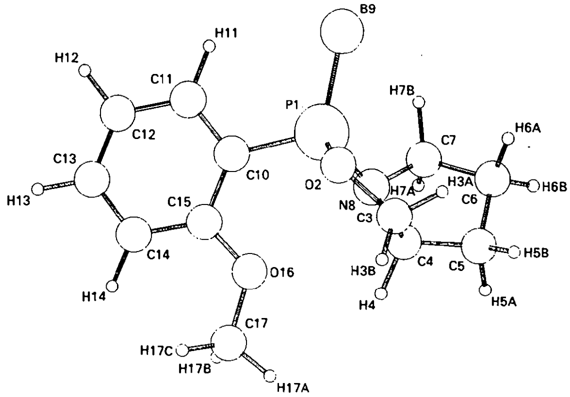


Fig. 1. A view of the molecule (*PLUTO*; Motherwell & Clegg, 1978), showing the atom-numbering scheme. The H atoms of the borane group are not shown.

Experimental

The compound was obtained as described previously (Buono, Brunel, Faure & Pardigon, 1993) and was recrystallized twice from hexane.

Crystal data

$C_{12}H_{19}BNO_2P$
$M_r = 251.1$
Orthorhombic
$P2_12_12_1$
$a = 7.197\ (1)$ Å
$b = 8.270\ (1)$ Å
$c = 22.684\ (1)$ Å
$V = 1350.1\ (2)$ Å^3
$Z = 4$
$D_x = 1.24$ Mg m^{-3}

Cu $K\alpha$ radiation
$\lambda = 1.5418$ Å
Cell parameters from 30 reflections
$\theta = 15$–$35°$
$\mu = 1.706$ mm^{-1}
$T = 291$ K
Parallelepiped
0.37 × 0.20 × 0.18 mm
White