Table 1. *Fractional atomic coordinates and equivalent isotropic thermal parameters* (Å²)

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

	x	y	z	U_{eq}
O1	0.0825 (2)	0.7040 (2)	0.2957 (1)	0.032 (1)
O2	−0.5281 (2)	0.5810 (2)	0.3200 (2)	0.044 (1)
O3	−0.2181 (2)	0.7018 (2)	0.5323 (1)	0.035 (1)
O4	0.2055 (2)	0.4820 (2)	0.3787 (1)	0.035 (1)
C1	−0.1552 (2)	0.6860 (2)	0.3701 (1)	0.020 (1)
C2	−0.1740 (3)	0.8419 (2)	0.3523 (2)	0.024 (1)
C3	−0.3356 (3)	0.8855 (3)	0.3554 (2)	0.033 (1)
C4	−0.4304 (3)	0.8030 (3)	0.2897 (2)	0.037 (1)
C5	−0.4196 (3)	0.6519 (3)	0.3108 (2)	0.027 (1)
C6	−0.2639 (2)	0.5881 (3)	0.3159 (2)	0.021 (1)
C7	−0.2687 (3)	0.4501 (3)	0.3697 (2)	0.029 (1)
C8	−0.1845 (3)	0.4779 (3)	0.4586 (2)	0.026 (1)
C9	−0.0226 (3)	0.4407 (3)	0.4502 (2)	0.027 (1)
C10	0.0621 (3)	0.5170 (3)	0.3955 (2)	0.027 (1)
C11	0.0051 (2)	0.6411 (2)	0.3487 (1)	0.022 (1)
C12	−0.1888 (3)	0.6350 (3)	0.4666 (2)	0.023 (1)
C13	−0.0814 (3)	0.9316 (3)	0.4163 (2)	0.033 (1)
C14	−0.2144 (3)	0.5653 (3)	0.2173 (2)	0.031 (1)
C15	0.0330 (4)	0.3157 (3)	0.4994 (2)	0.042 (1)

Table 2. *Geometric parameters* (Å, °)

O1—C11	1.215 (3)	C4—C5	1.497 (4)
O2—C5	1.204 (3)	C5—C6	1.540 (3)
O3—C12	1.197 (3)	C6—C7	1.555 (4)
O4—C10	1.363 (3)	C6—C14	1.544 (3)
C1—C2	1.540 (3)	C7—C8	1.544 (4)
C1—C6	1.583 (3)	C8—C9	1.513 (4)
C1—C11	1.546 (3)	C8—C12	1.525 (3)
C1—C12	1.542 (3)	C9—C10	1.337 (3)
C2—C3	1.522 (4)	C9—C15	1.499 (4)
C2—C13	1.534 (4)	C10—C11	1.479 (3)
C3—C4	1.523 (4)		
C2—C1—C6	115.5 (2)	C5—C6—C14	106.0 (2)
C2—C1—C11	110.1 (2)	C7—C6—C14	111.8 (2)
C2—C1—C12	116.7 (2)	C6—C7—C8	105.8 (2)
C6—C1—C11	108.1 (2)	C7—C8—C9	111.5 (2)
C6—C1—C12	99.0 (2)	C7—C8—C12	103.2 (2)
C11—C1—C12	106.5 (2)	C9—C8—C12	105.5 (2)
C1—C2—C3	111.9 (2)	C8—C9—C10	118.3 (2)
C1—C2—C13	112.8 (2)	C8—C9—C15	118.5 (2)
C3—C2—C13	110.4 (2)	C10—C9—C15	123.2 (2)
C2—C3—C4	112.1 (2)	O4—C10—C9	121.3 (2)
C3—C4—C5	110.0 (2)	O4—C10—C11	116.6 (2)
O2—C5—C4	121.8 (2)	C9—C10—C11	122.1 (2)
O2—C5—C6	120.7 (2)	O1—C11—C1	122.1 (2)
C4—C5—C6	117.5 (2)	O1—C11—C10	120.5 (2)
C1—C6—C5	110.7 (2)	C1—C11—C10	117.3 (2)
C1—C6—C7	105.8 (2)	O3—C12—C1	128.6 (2)
C1—C6—C14	112.6 (2)	O3—C12—C8	127.4 (2)
C5—C6—C7	110.1 (2)	C1—C12—C8	103.9 (2)
C1—C2—C3—C4	−55.9 (3)	C8—C12—C1—C6	46.7 (2)
C2—C3—C4—C5	58.5 (3)	C12—C1—C6—C7	−33.0 (2)
C3—C4—C5—C6	−53.7 (3)	C1—C12—C8—C9	74.1 (3)
C4—C5—C6—C1	43.7 (3)	C12—C8—C9—C10	−43.5 (3)
C5—C6—C1—C2	−39.3 (3)	C8—C9—C10—C11	4.4 (4)
C6—C1—C2—C3	46.6 (3)	C9—C10—C11—C1	3.9 (3)
C1—C6—C7—C8	8.2 (3)	C10—C11—C1—C12	27.4 (2)
C6—C7—C8—C12	20.6 (3)	C11—C1—C12—C8	−65.3 (2)
C7—C8—C12—C1	−42.9 (3)		

All calculations were performed by the *SHELXTL-Plus* programs (Sheldrick, 1987) with an IBM-PC/AT computer. Absolute configuration was not determined because of the lack of anomalous scatterers.

Lists of structure factors, anisotropic thermal parameters and H-atom coordinates have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55940 (8 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: VS1002]

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Structure of 4-Nitrobenzyl *N*-(4-Nitrobenzyloxy)trifluoroacetimidate

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Abstract

The molecular structure of the title compound is characterized by the *cisoid* geometry of the oximino-ether residue.

Comment

In experiments that were directed to the synthesis of polyamine analogues, a series of condensations were carried out between primary alcohols and *N*-trifluoroacetamidooxyalkyl derivatives by the Mitsunobu reaction (Mitsunobu, 1981). It was hoped that the condensation would lead to *N*-alkyltrifluoroacetamidooxy derivatives. However, the sole

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products showed chemistry more to be expected from acetimidates. It is known that the Mitsunobu condensation between alcohols and acetamides leads to mixtures of *N*-alkylated acetamides and acetimidates (Maurer & Miller, 1982). The single product from the condensation of 4-nitrobenzyl alcohol and *N*-trifluoroacetyl-4-nitrobenzyloxyamine was crystallized for crystal-structure determination from 95% ethanol. The structure of the reaction product has been established as an *N*-oxyimidate derivative.

The oximino-ether residue has *cisoid* geometry and is quasi-planar. As a consequence, the angles N(3)—C(4)—O(5) [134.1 (5)°] and C(4)—O(5)—C(6) [119.7 (4)°] are larger than the expected values for an sp^2 C atom and an sp^3 O atom, respectively, to reduce steric hindrance. The N(3)═C(4) distance of 1.252 (9) Å is somewhat shorter than the average C═N distance found in oximes [$(C,H)_2$—C═N—OH 1.281 (13) Å (Allen *et al.*, 1987)]. The N(3)—O(2) distance of 1.397 (6) Å corresponds to a single N—O [N—O distance in C_2—N(sp^2)—O—C 1.397 (11) Å (Allen *et al.*, 1987)]. The conformation of the chain C(1) to C(6) can be described as +*ap* [C(7)—C(1)—O(2)—N(3) 173.3 (5)°], +*ap* [C(1)—O(2)—N(3)—C(4) 177.8 (6)°], +*sp* [O(2)—N(3)—C(4)—O(5) 4.1 (11)°], −*sc* [N(3)—C(4)—O(5)—C(6) −37.2 (12)°], −*ap* [C(4)—O(5)—C(6)—C(17) −155.5 (6)°]. The two planar phenyl rings [maximum deviation from best plane 0.006 (8) Å] make an angle of 34.7 (2)° to each other. The trifluoromethyl group shows rotational disorder which could not be described by undoubling of the F atoms. The highest peaks in the difference electron density are found in this region.

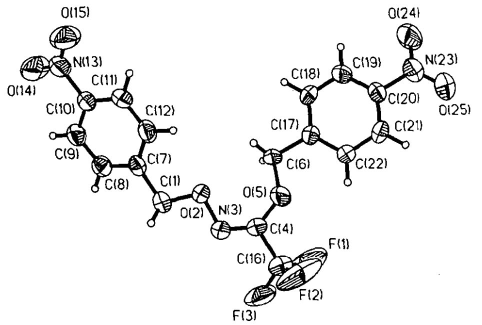

Fig. 1. View of the molecule with labelling. Thermal ellipsoids are shown at 50% probability levels; H atoms are drawn as small circles of arbitrary radii (*SHELXTL PC*; Siemens, 1990).

Experimental

Crystal data

$C_{16}H_{12}F_3N_3O_6$
M_r = 399.3
Triclinic
$P\overline{1}$
a = 7.333 (1) Å
b = 8.339 (1) Å
c = 15.616 (4) Å
α = 95.68 (1)°
β = 103.20 (2)°
γ = 107.62 (2)°
V = 871.4 (4) Å^3
Z = 2
D_x = 1.522 Mg m^{-3}

Cu *K*α radiation
λ = 1.54184 Å
Cell parameters from 20 reflections
θ = 7–18°
μ = 1.175 mm^{-1}
T = 289 K
Parallelepiped
0.35 × 0.15 × 0.10 mm
White
Crystal source: evaporation from 95% EtOH

Data collection

Siemens *P4-PC* diffractometer
2θ/θ scans
Absorption correction: none
2325 measured reflections
1790 independent reflections
1485 observed reflections [$F > 4\sigma(F)$]

$R_{\rm int}$ = 0.0226
$\theta_{\rm max}$ = 50.25°
h = −1 → 7
k = −8 → 8
l = −15 → 15
3 standard reflections monitored every 100 reflections intensity variation: 6%

Refinement

Refinement on *F*
Final *R* = 0.0709
wR = 0.0637
S = 1.02
1485 reflections
253 parameters
Riding model for H atoms: C—H 0.96 Å, fixed $U_{\rm iso}$ 0.08 Å^2

Unit weights applied
$(\Delta/\sigma)_{\rm max}$ = 0.002
$\Delta\rho_{\rm max}$ = 0.50 e Å^{-3}
$\Delta\rho_{\rm min}$ = −0.29 e Å^{-3}
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Data collection and data reduction: *XSCANS* (Siemens, 1992). Program package used to solve and refine structure: *SHELXTL PC* (Siemens, 1990). Refinement was by full-matrix least-squares methods.

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

$U_{\rm eq}$ is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	*y*	*z*	$U_{\rm eq}$
C(1)	0.2936 (10)	0.0744 (7)	0.0574 (4)	0.055 (3)
O(2)	0.3297 (7)	0.0876 (5)	0.1519 (3)	0.059 (2)
N(3)	0.3842 (8)	0.2617 (6)	0.1864 (3)	0.057 (3)
C(4)	0.4144 (9)	0.2916 (7)	0.2695 (4)	0.051 (3)
O(5)	0.4159 (7)	0.1947 (5)	0.3330 (3)	0.073 (2)
C(6)	0.2740 (10)	0.0232 (7)	0.3144 (4)	0.055 (3)
C(7)	0.2576 (8)	−0.1059 (7)	0.0151 (4)	0.046 (3)
C(8)	0.1750 (9)	−0.1517 (8)	−0.0769 (4)	0.055 (3)
C(9)	0.1404 (9)	−0.3136 (8)	−0.1219 (4)	0.056 (3)
C(10)	0.1884 (9)	−0.4308 (7)	−0.0724 (4)	0.050 (3)
C(11)	0.2721 (9)	−0.3905 (8)	0.0192 (4)	0.053 (3)
C(12)	0.3057 (9)	−0.2269 (8)	0.0622 (4)	0.053 (3)
N(13)	0.1483 (10)	−0.6048 (7)	−0.1198 (4)	0.068 (3)
O(14)	0.0463 (10)	−0.6459 (6)	−0.1957 (4)	0.116 (3)
O(15)	0.2159 (10)	−0.6988 (7)	−0.0797 (4)	0.108 (3)
C(16)	0.4804 (14)	0.4786 (9)	0.3125 (6)	0.077 (4)
F(1)	0.3715 (10)	0.5080 (6)	0.3600 (5)	0.177 (4)
F(2)	0.6531 (9)	0.5256 (6)	0.3694 (5)	0.162 (4)
F(3)	0.4936 (13)	0.5802 (6)	0.2585 (4)	0.204 (5)
C(17)	0.2479 (8)	−0.0230 (7)	0.4035 (4)	0.045 (3)
C(18)	0.1667 (9)	−0.1951 (7)	0.4069 (4)	0.056 (3)
C(19)	0.1341 (10)	−0.2434 (8)	0.4844 (4)	0.059 (3)

C(20)	0.1834 (9)	−0.1214 (8)	0.5586 (4)	0.047 (3)
C(21)	0.2628 (9)	0.0491 (8)	0.5576 (4)	0.056 (3)
C(22)	0.2962 (9)	0.0986 (7)	0.4787 (4)	0.051 (3)
N(23)	0.1450 (9)	−0.1723 (9)	0.6429 (4)	0.068 (3)
O(24)	0.0574 (10)	−0.3218 (8)	0.6410 (3)	0.112 (3)
O(25)	0.2031 (9)	−0.0636 (7)	0.7094 (3)	0.097 (3)

Table 2. *Geometric parameters* (Å, °)

C(1)—O(2)	1.425 (7)	C(1)—C(7)	1.500 (9)
O(2)—N(3)	1.397 (6)	N(3)—C(4)	1.252 (9)
C(4)—O(5)	1.340 (8)	C(4)—C(16)	1.518 (9)
O(5)—C(6)	1.447 (6)	C(6)—C(17)	1.518 (9)
C(7)—C(8)	1.390 (8)	C(7)—C(12)	1.388 (10)
C(8)—C(9)	1.380 (9)	C(9)—C(10)	1.382 (10)
C(10)—C(11)	1.383 (8)	C(10)—N(13)	1.474 (8)
C(11)—C(12)	1.383 (9)	N(13)—O(14)	1.201 (8)
N(13)—O(15)	1.200 (9)	C(16)—F(1)	1.266 (14)
C(16)—F(2)	1.290 (10)	C(16)—F(3)	1.251 (10)
C(17)—C(18)	1.389 (8)	C(17)—C(22)	1.374 (8)
C(18)—C(19)	1.361 (9)	C(19)—C(20)	1.365 (8)
C(20)—C(21)	1.367 (9)	C(20)—N(23)	1.484 (9)
C(21)—C(22)	1.388 (9)	N(23)—O(24)	1.211 (9)
N(23)—O(25)	1.208 (8)		
O(2)—C(1)—C(7)	109.8 (5)	C(1)—O(2)—N(3)	105.9 (4)
O(2)—N(3)—C(4)	112.8 (5)	N(3)—C(4)—O(5)	134.1 (5)
N(3)—C(4)—C(16)	116.0 (6)	O(5)—C(4)—C(16)	109.7 (6)
C(4)—O(5)—C(6)	119.7 (4)	O(5)—C(6)—C(17)	107.1 (4)
C(1)—C(7)—C(8)	117.4 (6)	C(1)—C(7)—C(12)	123.8 (5)
C(8)—C(7)—C(12)	118.7 (6)	C(7)—C(8)—C(9)	121.5 (6)
C(8)—C(9)—C(10)	117.8 (5)	C(9)—C(10)—C(11)	122.6 (6)
C(9)—C(10)—N(13)	118.1 (5)	C(11)—C(10)—N(13)	119.3 (6)
C(10)—C(11)—C(12)	118.1 (6)	C(7)—C(12)—C(11)	121.2 (5)
C(10)—N(13)—O(14)	118.1 (6)	C(10)—N(13)—O(15)	118.1 (5)
O(14)—N(13)—O(15)	123.7 (6)	C(4)—C(16)—F(1)	112.8 (7)
C(4)—C(16)—F(2)	111.3 (7)	F(1)—C(16)—F(2)	102.7 (7)
C(4)—C(16)—F(3)	114.4 (7)	F(1)—C(16)—F(3)	108.8 (9)
F(2)—C(16)—F(3)	106.1 (7)	C(6)—C(17)—C(18)	117.7 (5)
C(6)—C(17)—C(22)	122.5 (5)	C(18)—C(17)—C(22)	119.8 (6)
C(17)—C(18)—C(19)	120.2 (5)	C(18)—C(19)—C(20)	119.4 (6)
C(19)—C(20)—C(21)	122.1 (6)	C(19)—C(20)—N(23)	119.8 (6)
C(21)—C(20)—N(23)	118.1 (5)	C(20)—C(21)—C(22)	118.6 (5)
C(17)—C(22)—C(21)	119.9 (5)	C(20)—N(23)—O(24)	117.6 (6)
C(20)—N(23)—O(25)	118.6 (6)	O(24)—N(23)—O(25)	123.7 (7)

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Lists of structure factors, anisotropic displacement coefficients, H-atom coordinates and least-squares-planes data have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55937 (12 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: LI1038]

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Orthorhombic Form of Thiopurinol: 1,5-Dihydro-4*H*-pyrazolo[3,4-*d*]pyrimidine-4-thione

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Abstract

Thiopurinol crystallizes in two forms. The crystal structure of the monoclinic form has been reported [Gadret, Goursolle & Leger (1974). *Acta Cryst.* **B30**, 1598–1602]. The orthorhombic form reported here has a hydrogen-bonded layered structure similar to the monoclinic form but differs from it in the stacking pattern of the purine bases. The interlayer separation (3.292 Å) is slightly smaller than that in the monoclinic form (3.426 Å). The H atom on the diazole ring is bonded to N(9). The relative magnitudes of the two exocyclic bond angles at N(9) subtended by H(9) are similar to those in the monoclinic form and in allopurinol, but differ from those in hypoxanthine, the related normal nucleobase. This trend for N(8)-purines is corroborated by *ab initio* molecular-orbital calculations and a literature search for related structures *via* the Cambridge Structural Database [Allen, Kennard & Taylor (1983). *Acc. Chem. Res.* **16**, 146–153].

Comment

The title compound (I*a*) is the thio analog of allopurinol (I*b*) and possesses very similar biochemical and pharmacological properties. Thus, both allopurinol and thiopurinol riboside monophosphates inhibit guanosine monophosphate reductase and, therefore, affect the synthesis of adenosine triphosphate from guanine (Looker, Marr & Berens, 1986). Both inhibit ribonucleic acid biosynthesis thus affecting protein synthesis (Looker *et al.*, 1986). Both are potent

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