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9-(2-Acetoxyethoxymethyl)-2-formamido-6-(*p*-tolylsulfonyloxy)purine

Sergey Belyakov,* Martins Ikaunieks and Marina Madre

Latvian Institute of Organic Synthesis, Riga, LV 1006, Latvia

Correspondence e-mail: serg@osi.lv

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Key indicators

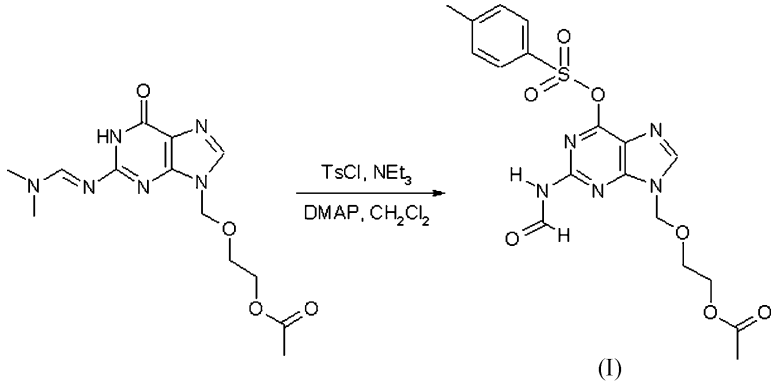
Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.004 Å
R factor = 0.056
wR factor = 0.129
Data-to-parameter ratio = 16.1

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

The title compound, $C_{18}H_{19}N_5O_7S$, can be considered as a synthetic analogue of nucleosides. The molecule displays an *anti* conformation. The occurrence of N—H···O hydrogen bonds results in the formation of centrosymmetric dimers. The crystal packing is characterized by π–π stacking interactions between the purine systems.

Comment

The present crystallographic analysis of the title compound, (I), extends our ongoing investigation of the synthesis of C-6 aryl purine derivatives using the Suzuki–Miyaura reaction, *i.e.* the Pd-mediated cross-coupling of haloaromatics or aryltriflates with an aryl boronic acid (Miyaura & Suzuki 1995; Suzuki, 1999). This method has led to the development of several biologically active nucleoside analogues, which are generally prepared using 6-chloropurines as substrates (Česnek *et al.*, 2000). Commercially available 6-chloroguanosine derivatives are expensive, but their preparation *via* chlorination of 6-oxopurines proceeds mostly with low yields. Therefore, the development of O^6-tosylated guanine derivatives as alternative substrates for cross-coupling reactions is important (Lakshman *et al.*, 2002). We report here the single-crystal structure of an O^6-tosylate derivative, (I), of acyclic guanosine, as a typical example of the class of intermediates synthesized by tosylation of N^2-amidine-protected 9-(2-acetoxyethoxymethyl)guanine and related analogues. The chemical structures of O^6-tosylates of acyclic guanosine analogues have not hitherto been confirmed in the literature by single-crystal X-ray diffraction analysis.



(I)

The molecular structure of (I) is shown in Fig. 1. The bond lengths and angles of (I) compare well with those of related compounds extracted from the Cambridge Structural Database (CSD, Version 5.26; Allen, 2002). Only 18 entries containing 9-oxymethylpurine derivatives could be found.

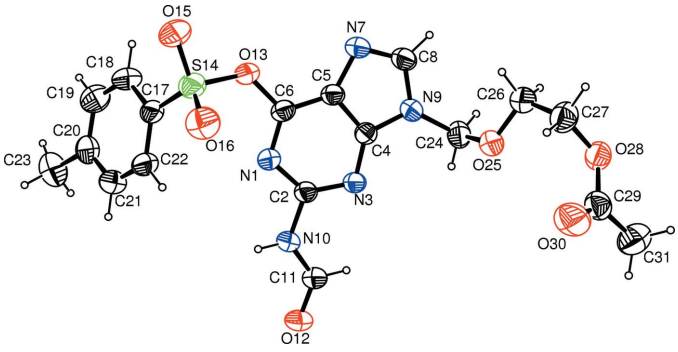


Figure 1
The molecular structure of (I), showing 50% probability displacement ellipsoids and the atom-numbering scheme. H atoms are represented by spheres of arbitrary radii.

Selected torsion angles for (I) are reported in Table 1. The value of 77.1 (3)° observed for C8—N9—C24—O25 indicates that the purine system exhibits the *anti* conformation across the pseudo-glycosidic bond.

The packing of the molecules in the crystal structure of (I) viewed down the *a* axis is shown in Fig. 2. Intermolecular N—H···O hydrogen bonds result in the formation of centrosymmetric dimers. Slipped π–π stacking interactions are observed between purine systems related by an inversion centre (Fig. 2). The distance between the planes of these overlapped purine fragments is 3.358 (3) Å, whereas the centroid-to-centroid distance is 3.658 Å [symmetry code: $-x+2, -y+1, -z+1$].

Experimental

4-Toluenesulfonyl chloride (0.25 g, 1.3 mmol) was added at 273 K to a solution containing 9-(2-acetoxyethoxymethyl)-2-(*N*,*N*-dimethylimidoformamido)-6-oxopurine (0.16 g, 0.5 mmol), DMAP (4-dimethylaminopyridine; 15.3 mg, 0.13 mmol), NEt_3 (0.19 g, 1.85 mmol) and dichloromethane (10 ml). After the mixture had been allowed to reach ambient temperature, stirring was continued for 4 h. It was then washed with aqueous $NaHCO_3$ (1 × 2 ml) and water (2 × 2 ml). The organic layer was dried ($MgSO_4$) and evaporated under reduced pressure. The residue was dissolved in dichloromethane and subjected to column chromatography (silica gel, CH_2Cl_2–EtOH 100:1), and crystallized from ethanol (yield 0.29 g, 79%; m.p. 436–438 K). Spectroscopic analysis: ^{1}H NMR (200 MHz, DMSO-d_6, δ): 11.26 (*d*, 1H, *J* = 10.3 Hz, NH), 9.08 (*d*, 1H, *J* = 10.3 Hz, CH), 8.58 (*s*, 1H, CH), 8.09 (*d*, 2H, C_6H_4), 7.51 (*d*, 2H, C_6H_4), 5.59 (*s*, 2H, NCH_2), 4.09–4.01 (*m*, 2H, CH_2), 3.75–3.68 (*m*, 2H, CH_2), 2.43 (*s*, 3H, CH_3), 1.88 (*s*, 3H, OAc). Analysis calculated for $C_{18}H_{19}N_5O_7S$: C 48.10, H 4.26, N 15.58%: found: C 48.47, H 4.31, N 15.73%. Crystals of (I) suitable for X-ray structure analysis were obtained by slow evaporation of an EtOH–H_2O (2:1) solution at room temperature.

Crystal data

$C_{18}H_{19}N_5O_7S$
M_r = 449.44
Monoclinic, $P2_1/n$
a = 10.4397 (3) Å
b = 10.8046 (3) Å
c = 17.8259 (7) Å
β = 92.5932 (12)°
V = 2008.65 (11) Å^3
Z = 4
D_x = 1.486 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 4435 reflections
θ = 1.0–27.5°
μ = 0.21 mm^{-1}
T = 293 K
Needle, colourless
0.31 × 0.08 × 0.07 mm

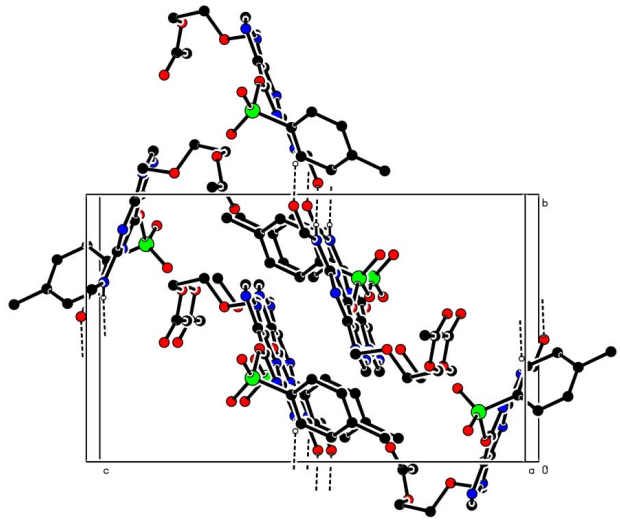


Figure 2
A packing diagram for (I), viewed down the *a* axis. Dashed lines show hydrogen bonding. For the sake of clarity, H atoms not involved in the hydrogen bonds have been omitted.

Data collection

Nonius KappaCCD area-detector diffractometer
φ and ω scans
Absorption correction: none
8435 measured reflections
4539 independent reflections
3215 reflections with $I > 2\sigma(I)$
R_{int} = 0.036
θ_{max} = 27.5°
h = −13 → 13
k = −12 → 13
l = −23 → 23

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.056
$wR(F^2)$ = 0.129
S = 1.13
4539 reflections
282 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0341P)^2 + 1.0912P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.22 e Å^{-3}
$\Delta\rho_{min}$ = −0.26 e Å^{-3}

Table 1
Selected torsion angles (°).

N1—C2—N10—C11	169.5 (2)	C8—N9—C24—O25	77.6 (3)
C2—N10—C11—O12	178.6 (2)	N9—C24—O25—C26	−84.9 (3)
C6—O13—S14—O15	167.0 (2)	C24—O25—C26—C27	−170.8 (2)
C6—O13—S14—O16	39.0 (2)	O25—C26—C27—O28	64.6 (3)
C6—O13—S14—C17	−79.6 (2)	C26—C27—O28—C29	−115.3 (3)
O13—S14—C17—C18	−82.3 (2)	C27—O28—C29—O30	−2.6 (4)
O13—S14—C17—C22	100.1 (2)	C27—O28—C29—C31	179.7 (2)
C4—N9—C24—O25	−94.9 (3)		

Table 2
Hydrogen-bond geometry (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N10—H10···O12^{i}	0.86	2.08	2.928 (3)	171

Symmetry code: (i) $-x+2, -y+2, -z+1$.

All H atoms were introduced in calculated positions and treated as riding atoms, with C—H distances of 0.93 (aromatic), 0.96 (methyl)

and 0.97 Å (CH_2), and N—H = 0.86 Å, with U_{iso}(H) = 1.2U_{eq}(aromatic C, CH_2 or N) and 1.5U_{eq}(methyl C).

Data collection: *KappaCCD Server Software* (Nonius, 1999); cell refinement: *HKL SCALEPACK* (Otwinowski & Minor 1997); data reduction: *DENZO* (Otwinowski & Minor, 1997) and *SCALEPACK*; program(s) used to solve structure: *DIRDIF96* (Beurskens *et al.*, 1996); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEPIII* (Burnett & Johnson, 1996) and *PLATON* (Spek, 2003); software used to prepare material for publication: *MAXUS* (Mackay *et al.*, 1999) and *SHELXL97*.

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