Experimental

The title compound was obtained from the Sigma Chemical Company. Crystals were grown by the diffusion method from an aqueous acetonitrile solution of the compound.

Crystal data

$C_{30}H_{24}N_2O_9$
$M_r = 556.51$
Monoclinic
$P2$
$a = 14.202\,(2)$ Å
$b = 5.737\,(3)$ Å
$c = 33.319\,(5)$ Å
$\beta = 92.93\,(2)°$
$V = 2711.5\,(15)$ Å^3
$Z = 4$
$D_x = 1.363$ Mg m^{-3}
D_m not measured

Cu $K\alpha$ radiation
$\lambda = 1.5418$ Å
Cell parameters from 25 reflections
$\theta = 10$–$25°$
$\mu = 0.855$ mm^{-1}
$T = 293\,(2)$ K
Plate
0.90 × 0.20 × 0.05 mm
Colourless

Data collection

Enraf–Nonius CAD-4 diffractometer
ω–2θ scans
Absorption correction: none
6192 measured reflections
5536 independent reflections
4265 reflections with $I > 2\sigma(I)$

$R_{\rm int} = 0.032$
$\theta_{\rm max} = 69.9°$
$h = 0 \rightarrow 16$
$k = 0 \rightarrow 6$
$l = -40 \rightarrow 40$
3 standard reflections every 100 reflections intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.041$
$wR(F^2) = 0.117$
$S = 1.055$
5491 reflections
789 parameters
H atoms constrained
$w = 1/[\sigma^2(F_o^2) + (0.1P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} = 0.009$
$\Delta\rho_{\rm max} = 0.278$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.235$ e Å^{-3}

Extinction correction: *SHELXL*93 (Sheldrick, 1993)
Extinction coefficient: 0.0016 (3)
Scattering factors from *International Tables for Crystallography* (Vol. C)
Absolute structure: Flack (1983)
Flack parameter = 0.15 (22)

Table 1. *Selected torsion angles (°)*

C2*A*—N1*A*—C1′*A*—O4′*A*	−154.8 (3)
O4′*A*—C1′*A*—C2′*A*—C3′*A*	−27.1 (3)
C1′*A*—C2′*A*—C3′*A*—C4′*A*	37.5 (3)
C2′*A*—C3′*A*—C4′*A*—O4′*A*	−35.1 (3)
C2′*A*—C1′*A*—O4′*A*—C4′*A*	5.5 (3)
C3′*A*—C4′*A*—O4′*A*—C1′*A*	18.9 (3)
O4′*A*—C4′*A*—C5′*A*—O5′*A*	−60.8 (4)
C3′*A*—C4′*A*—C5′*A*—O5′*A*	56.7 (4)
C2*B*—N1*B*—C1′*B*—O4′*B*	−156.8 (3)
O4′*B*—C1′*B*—C2′*B*—C3′*B*	−22.7 (3)
C1′*B*—C2′*B*—C3′*B*—C4′*B*	34.1 (3)
C2′*B*—C3′*B*—C4′*B*—O4′*B*	−34.1 (3)
C2′*B*—C1′*B*—O4′*B*—C4′*B*	1.5 (3)
C3′*B*—C4′*B*—O4′*B*—C1′*B*	20.8 (3)
O4′*B*—C4′*B*—C5′*B*—O5′*B*	−62.3 (4)
C3′*B*—C4′*B*—C5′*B*—O5′*B*	55.4 (4)

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989). Data reduction: *CAD*-4 *Software*. Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *INSIGHT*II (Biosym Technologies, 1995) and *Xtal_GX* (Hall & du Boulay, 1995). Software used to prepare material for publication: *SHELXL*93.

We thank DST and CSIR, India, for financial assistance.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: VJ1093). Services for accessing these data are described at the back of the journal.

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2′-*O*-Tosyladenosine

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Abstract

In the title compound, 2′-*O*-tosyl(toluenesulfonyl)adenosine, $C_{17}H_{19}N_5O_6S$, the adenine base is in the *syn* conformation with a glycosidic torsion angle of 62.7 (4)°. The ribose sugar adopts the envelope conformation (^2E). The tosyl moiety is nearly parallel to the base. Both Watson–Crick and Hoogsteen sites of the adenine bases are involved in intermolecular hydrogen bonds.

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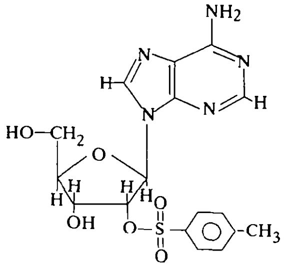
Comment

Chemically modified nucleosides and nucleotides are used extensively as probes to study enzyme mechanisms and as chemotherapeutic agents (Suhadolnik, 1970; Saenger & Suck, 1973; Neidle *et al.*, 1996). For sometime we have been interested in the crystal structures of modified nucleosides and nucleotides to evaluate the influence of various base and ribose modifications (Gautham *et al.*, 1983; Mande *et al.*, 1988, 1989). The structural study of the title compound, (I), was taken up to examine the effect of the bulky tosyl group on the conformation of the nucleoside molecule.



(I)

The atomic numbering and conformation of (I) is shown in Fig. 1. The glycosyl torsion angle C4—N9—C1′—O4′ is 62.7 (4)° indicating a *syn* conformation. The sugar ring has a C2′-*endo* envelope conformation. C1′, C3′, C4′ and O4′ are coplanar to within 0.029 Å and C2′ is displaced by 0.59 Å from the four-atom plane on the same side as C5′. The pseudorotation parameters (Altona & Sundaralingam, 1972) are P = 172.3 (7)° and τ_m = 39.1 (4)°. The exocyclic torsion angle about the C4′—C5′ bond is g^+. There is intramolecular stacking between the adenine base and the tosyl moiety. The average base–tosyl moiety interatomic distance is 3.6 Å.

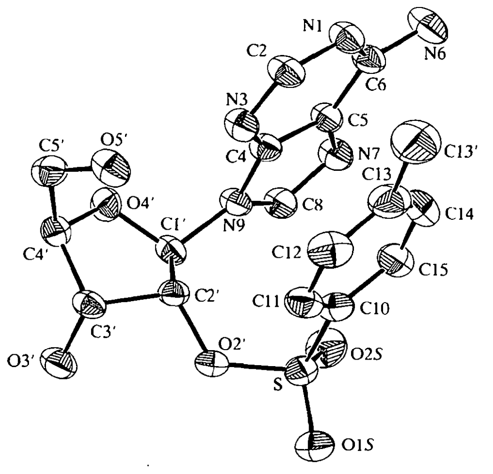


Fig. 1. Atomic numbering and molecular conformation of (I) showing 50% probability displacement ellipsoids. H atoms are omitted for clarity.

There is an intramolecular hydrogen bond between N3 of adenine and O5′ of ribose. Similar hydrogen bonds have been found in several previous crystal structures, stabilizing the *syn*, g^+ geometry of the molecule (Krishnan & Seshadri, 1993; Padiyar & Seshadri, 1998). The exocyclic amino-N atom N6 is hydrogen-bonded to N1 and N7 of symmetry-related molecules. Thus both Watson–Crick and Hoogsteen sites of the adenine base are involved in hydrogen bonding. There is also intramolecular stacking between the adenine base and the tosyl moiety along the a axis of the crystal lattice. Ribose hydroxyl-O atom O3′ forms a hydrogen bond with O5′ of a symmetry-related molecule in the unit cell. Hydrogen-bonding geometry is summarized in Table 2.

Experimental

The title compound was obtained from the Sigma Chemical Company. Crystals were grown by the liquid-diffusion method from a water–dimethyl sulfoxide solution of the compound.

Crystal data

$C_{17}H_{19}N_5O_6S$
M_r = 421.43
Monoclinic
$P2_1$
a = 7.359 (3) Å
b = 7.873 (3) Å
c = 16.098 (4) Å
β = 96.00 (2)°
V = 927.6 (6) Å^3
Z = 2
D_x = 1.509 Mg m^{-3}
D_m not measured

Cu $K\alpha$ radiation
λ = 1.5418 Å
Cell parameters from 25 reflections
θ = 6–12°
μ = 1.984 mm^{-1}
T = 293 (2) K
Parallelepiped
0.60 × 0.30 × 0.20 mm
Colourless

Data collection

Enraf–Nonius CAD-4 diffractometer
ω–2θ scans
Absorption correction: ψ scan (North *et al.*, 1968)
$T_{\min}$ = 0.635, $T_{\max}$ = 0.672
1936 measured reflections
1936 independent reflections

1881 reflections with $I > 2\sigma(I)$
$\theta_{\max}$ = 71.93°
$h = -9 \rightarrow 9$
$k = 0 \rightarrow 9$
$l = 0 \rightarrow 19$
3 standard reflections every 100 reflections intensity decay: none

Refinement

Refinement on F^2
$R(F)$ = 0.057
$wR(F^2)$ = 0.136
S = 1.091
1936 reflections
283 parameters
H atoms: see text
$w = 1/[\sigma^2(F_o^2) + (0.0482P)^2 + 0.1143P]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max}$ = 0.001
$\Delta\rho_{\max}$ = 0.935 e Å^{-3}
$\Delta\rho_{\min}$ = −0.663 e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)
Absolute structure: Flack (1983)
Flack parameter = 0.02 (3)

Table 1. *Selected torsion angles (°)*

N9—C1′—C2′—O2′	−87.8 (4)	C3′—C4′—O4′—C1′	−7.7 (4)
O4′—C1′—C2′—C3′	35.4 (3)	O4′—C4′—C5′—O5′	−80.9 (3)
C3′—C2′—O2′—S	−172.0 (2)	C3′—C4′—C5′—O5′	38.5 (4)
C1′—C2′—O2′—S	72.8 (3)	C2′—O2′—S—OS2	−69.4 (3)
C1′—C2′—C3′—C4′	−38.8 (3)	C2′—O2′—S—OS1	162.8 (3)
C2′—C3′—C4′—O4′	29.1 (3)	C2′—O2′—S—C10	46.4 (3)
C2′—C1′—O4′—C4′	−17.4 (3)		

Table 2. *Hydrogen-bonding geometry (Å, °)*

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N6—H61···N7^{i}	0.86	2.14	2.990 (5)	170
N6—H62···N1^{ii}	0.86	2.16	2.952 (5)	154
O3′—HO3′···O5′^{iii}	0.92 (5)	1.87 (5)	2.778 (4)	171 (5)
O5′—HO5′···N3	0.68 (6)	2.10 (6)	2.780 (4)	176 (7)

Symmetry codes: (i) $2 - x, \frac{1}{2} + y, 1 - z$; (ii) $2 - x, y - \frac{1}{2}, 1 - z$; (iii) $1 - x, y - \frac{1}{2}, -z$.

All H atoms were located riding on their parent atoms, and their occupancies and *U* values were refined.

Data collection: *CAD*-4 (Enraf–Nonius, 1985). Cell refinement: *CAD*-4 (Enraf–Nonius, 1985). Data reduction: *Structure Determination Package* (Frenz, 1982). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *Xtal_GX* (Hall & du Boulay, 1995). Software used to prepare material for publication: *SHELXL*93.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: VJ1090). Services for accessing these data are described at the back of the journal.

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2-Bromo-2,3-diphenylmethano-2,3-dihydronaphthoquinone

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Abstract

In the title compound, a diphenylhomonaphthoquinone, $C_{23}H_{15}BrO_2$, the quinone frame adopts a slightly boat-shaped conformation, with folding angles of 11 (3) and 14 (3)°. The severe steric congestion between the *endo*-phenyl group and the quinone moiety results in considerable freezing of the aromatic ring.

Comment

The thermal ring-opening of cyclopropanes is much influenced by the spatial arrangement of adjacent unsaturated substituents such as C═C, C═O and phenyl groups, because the cyclopropane σ-bond is recognized as being greatly analogous to a C═C double bond (Meijere, 1979; Wong *et al.*, 1989). The most favourable orbital interaction is geometrically attained in the bisected conformation between the cyclopropane ring and the planes of the unsaturated substituents (Tidwell, 1985; Crabb & Patel, 1992).

Thermolysis of the title compound, (I), at 373 K yields the diphenylmethylene-substituted dihydronaphthoquinone, (II), *via* cyclopropane ring-opening accompanied by a simultaneous bromide migration (Oshima *et al.*, 1994). A preliminary kinetic study of the thermolysis of (I) and of *p*-substituted homologues reveals that the *exo*-aromatic substituents affect the rates much more than the corresponding *endo*-ones. The logarithmic correlation of the rate constants ($k\,\mathrm{s}^{-1}$ at 373 K in toluene) with the Brown σ^+ (Brown & Okamoto, 1958) was $\log k = -0.79\sigma^+ - 4.39$ ($r = 0.999$) for the five *endo*-aromatic substituents (*p*-CH_3O, *p*-CH_3, *p*-H, *p*-Cl, *p*-NO_2), while the more pronounced substituent effects were observed for the corresponding *exo*-substituents, for which $\log k = -1.90\sigma^+ - 4.23$ ($r = 0.999$). The negative ρ values (−0.79 and −1.90) and the correlation with σ^+ imply that the electron-donating π-participation of the aromatic rings to the breaking cyclopropane bond plays an important role in the bromide-releasing ring-