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Supplementary data for this paper are available from the IUCr electronic archives (Reference: NA1362). Services for accessing these data are described at the back of the journal.

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## An *N*-Substituted 6,7-Benzocoumarin-8,9-aziridine Derivative

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### Abstract

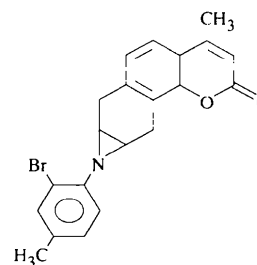
In the title compound, 8-(2-bromo-4-methylphenyl)-4-methyl-2,7,7a,8,8a,9-hexahydropyrano[2',3':1,2]naphth-[6,7]aziridin-2-one, C<sub>21</sub>H<sub>18</sub>BrNO<sub>2</sub>, the tetrahydrobenzene ring adopts a flattened-boat conformation. The aziridine plane forms dihedral angles of 80.4 (1) and 59.1 (2)°

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with the tetrahydrobenzene and *N*-phenyl substituent ring planes, respectively. The crystal structure is stabilized by weak C—H···O intermolecular hydrogen bonds and  $\pi$ – $\pi$  stacking interactions of the coumarin ring.

### Comment

The title compound is a newly synthesized member of the aziridine family. The aziridine ring is a versatile building block for organic synthesis, not only because the ring opening of aziridines provides a convenient entry to the stereoselective preparation of functionalized amino compounds, but also because exocyclic *N*-substituents modulate the properties and reactivity of the three-membered ring (Pearson *et al.*, 1996; Tanner, 1994). Because of their high reactivity, aziridines serve as useful intermediates in the synthesis of several natural products, such as mitomycin, crinine and reframidine (Kametani & Honda, 1986). The structural study of the title compound, (I), was undertaken in order to elucidate the molecular conformation and packing arrangement.



(I)

The bond lengths and angles in the structure agree with those observed in aziridine and coumarin derivatives (Chinnakali *et al.*, 1997, 1998; Kumar *et al.*, 1997). The N atom has pyramidal bonding geometry. In the coumarin ring system, the pyran ring is planar, with a maximum deviation of 0.030 (3) Å for C2; the dihedral angle between the benzene and pyran rings is 1.85 (9)°. The tetrahydrobenzene ring adopts a flattened-boat conformation with C12 and C15 deviating from the plane of C7, C8, C13 and C14 by 0.117 (4) and 0.110 (3) Å, respectively. The asymmetry parameters are  $\Delta C_s(C12) = 0.010(1)$  and  $\Delta C_s(C7-C8) = 0.008(1)$  (Nardelli, 1983). The best plane through the tetrahydrobenzene ring makes a dihedral angle of 2.51 (8)° with the benzene ring. The aziridine plane forms dihedral angles of 80.4 (1) and 59.1 (2)°, respectively, with the best plane through the tetrahydrobenzene and substituent phenyl rings. In the crystal, the carbonyl O atom is involved in a weak C—H···O intermolecular hydrogen bond [C19···O11<sup>i</sup> 3.412 (4) Å and C19—H19···O11<sup>i</sup> 156 (2)°; symmetry code: (i)  $x - \frac{1}{2}, -y - \frac{1}{2}, -z$ ]; the coumarin rings of the molecules are stacked 3.474 (3) Å apart, an optimum distance for  $\pi$ – $\pi$  stacking interactions.

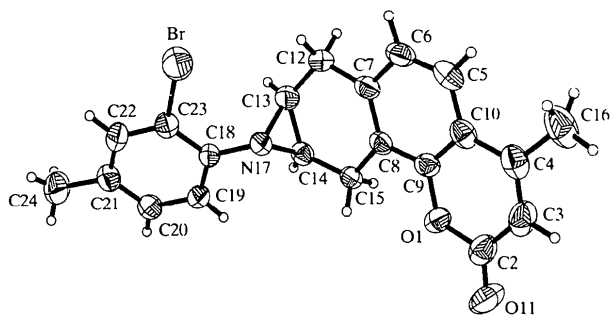


Fig. 1. The structure of the title compound showing 50% probability displacement ellipsoids and the atom-numbering scheme. H atoms are displayed as small circles of arbitrary radii.

4056 reflections  
298 parameters  
All H atoms refined  
 $w = 1/[\sigma^2(F_o^2) + (0.0356P)^2 + 2.3073P]$   
where  $P = (F_o^2 + 2F_c^2)/3$

Scattering factors from  
*International Tables for  
Crystallography* (Vol. C)

Table 1. Selected geometric parameters (Å, °)

C7—C12	1.503 (4)	C13—C14	1.481 (4)
C8—C15	1.507 (4)	C14—N17	1.467 (3)
C12—C13	1.494 (4)	C14—C15	1.498 (4)
C13—N17	1.478 (3)	N17—C18	1.420 (3)
C18—N17—C14	118.4 (2)	C14—N17—C13	60.4 (2)
C18—N17—C13	117.5 (2)		
C12—C7—C8—C15	1.0 (4)	C12—C13—C14—C15	1.8 (4)
C8—C7—C12—C13	9.5 (4)	C13—C14—C15—C8	8.4 (4)
C7—C12—C13—C14	-10.6 (4)	C7—C8—C15—C14	-9.9 (4)

## Experimental

8-(2-Bromo-4-methylanilino)-9-hydroxy-4-methyl-7,8,9,10-tetrahydro-7,8-benzocoumarin (0.5 g, 1.207 mmol) in benzene (30 ml) was stirred with 1.5 equivalents of *p*-toluenesulfonyl chloride, 0.2 equivalents of tetra-*n*-butylammonium hydrogen sulfate and 5 ml of 50% NaOH solution at room temperature. After completion of the reaction, the organic layer was separated and washed well with water, dried over anhydrous MgSO<sub>4</sub>, and the solvent removed under vacuum; chromatographic purification of the residue furnished 0.480 g of pale-yellow crystalline solid (Sriraghavan & Ramakrishnan, 1998). Single crystals of the compound were obtained by slow evaporation from a methanol/chloroform (1:1) solvent system.

### Crystal data

C <sub>21</sub> H <sub>18</sub> BrNO <sub>2</sub>	Mo K $\alpha$ radiation
$M_r = 396.27$	$\lambda = 0.71073 \text{ \AA}$
Orthorhombic	Cell parameters from 7584 reflections
<i>Pbca</i>	$\theta = 2.79\text{--}27.50^\circ$
$a = 8.2983 (1) \text{ \AA}$	$\mu = 2.342 \text{ mm}^{-1}$
$b = 14.6086 (2) \text{ \AA}$	$T = 293 (2) \text{ K}$
$c = 29.1258 (4) \text{ \AA}$	Thin plate
$V = 3530.82 (8) \text{ \AA}^3$	$0.62 \times 0.40 \times 0.04 \text{ mm}$
$Z = 8$	Light yellow
$D_x = 1.491 \text{ Mg m}^{-3}$	
$D_m$ not measured	

### Data collection

Siemens SMART CCD area-detector diffractometer	4060 independent reflections
$\omega$ scans	2665 reflections with $I > 2\sigma(I)$
Absorption correction: empirical (SADABS; Sheldrick, 1996a)	$R_{\text{int}} = 0.059$
$T_{\text{min}} = 0.561$ , $T_{\text{max}} = 0.911$	$\theta_{\text{max}} = 27.5^\circ$
21 549 measured reflections	$h = -10 \rightarrow 10$
	$k = -18 \rightarrow 18$
	$l = -37 \rightarrow 23$

### Refinement

Refinement on $F^2$	$(\Delta/\sigma)_{\text{max}} < 0.001$
$R[F^2 > 2\sigma(F^2)] = 0.048$	$\Delta\rho_{\text{max}} = 0.243 \text{ e \AA}^{-3}$
$wR(F^2) = 0.109$	$\Delta\rho_{\text{min}} = -0.503 \text{ e \AA}^{-3}$
$S = 1.065$	Extinction correction: none

The data collection covered over a hemisphere of reciprocal space by a combination of three sets of exposures; each set had a different  $\varphi$  angle (0, 88 and 180°) for the crystal and each exposure of 30 s covered 0.3° in  $\omega$ . The crystal-to-detector distance was 4 cm and the detector swing angle was -35°. Coverage of the unique set is over 99% complete. Crystal decay was monitored by repeating 30 initial frames at the end of data collection and analysing the duplicate reflections, and was found to be negligible. The structure was solved by direct methods and refined by full-matrix least-squares techniques. All H atoms were located from a difference Fourier map and refined isotropically.

Data collection: SMART (Siemens, 1996b). Cell refinement: SAINT (Siemens, 1996a). Data reduction: SAINT. Program(s) used to solve structure: SHELXTL (Sheldrick, 1996b). Program(s) used to refine structure: SHELXTL. Molecular graphics: SHELXTL. Software used to prepare material for publication: SHELXTL and PARST (Nardelli, 1995).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: HA1215). Services for accessing these data are described at the back of the journal.

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### *N*-(3-Hydroxyphenyl)-*p*-toluenesulfonamide

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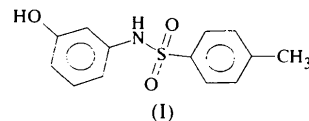
#### Abstract

In the title compound, C<sub>13</sub>H<sub>13</sub>NO<sub>3</sub>S, the dihedral angle between the toluene and phenol moieties is 69.48 (5)°. The molecules form columns linked by N—H···O and O—H···O hydrogen bonds.

#### Comment

Molecular recognition is central to the understanding of biological activity and enzymatic systems (Goswami & Ghosh, 1997). The title compound, (I), contains a potentially active sulfonamide moiety. Sulfonamides have been extensively used against many common gram-positive bacterial infections like pneumonia, meningitis, dysentery and urinary-tract infection (Kar, 1993). Hydrogen bonding is expected to play an important role

in governing the crystal structure of the title compound (Aoyama *et al.*, 1995). The X-ray structure determination was carried out in order to elucidate the molecular conformation and hydrogen bonding.



Bond lengths agree with other reported values (Allen *et al.*, 1987). The sum of the bond angles around the N1 atom [349 (1)°] indicates that it is in a pyramidal configuration. The dihedral angle between the toluene and phenol moieties is 69.48 (5)°. Chains of molecules along **b** are linked by O—H···O hydrogen bonds, and glide-related chains are interlinked by N—H···O hydrogen bonds (see Table 2 for details). These two chains form a column-like structure along the *b* axis, with the phenol groups occupying a plane and the toluene groups projecting outwards from it on either side. The toluene groups of neighbouring columns are arranged close to each other, but are not stacked to allow any  $\pi$ – $\pi$  interactions.

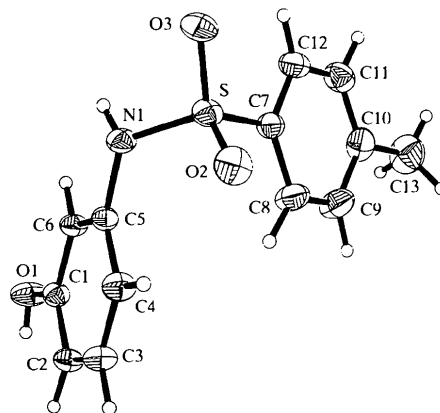


Fig. 1. The structure and atom-numbering scheme of the title compound, shown with 50% probability displacement ellipsoids.

#### Experimental

For the preparation of the title compound, *p*-toluenesulfonyl chloride (875 mg, 4.5 mmol) was added to a solution of *m*-aminophenol (500 mg, 4.5 mmol) and dry pyridine (0.5 ml) in dry CH<sub>2</sub>Cl<sub>2</sub> solvent at 283 K. The reaction mixture was stirred for 15 min at this temperature and for a further 1 h at room temperature. After the usual work-up, the desired compound was obtained in 80% yield (Kurita, 1974). Single crystals were grown by slow evaporation of a 4:1 dichloro-methane–methanol solution of the compound.

#### Crystal data

C<sub>13</sub>H<sub>13</sub>NO<sub>3</sub>S  
*M<sub>r</sub>* = 263.30

Mo *K*α radiation  
λ = 0.71073 Å

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