$$C_{14}H_{13}N_3O_2 \cdot H_2O$$

Table 1. *Selected geometric parameters (Å, °)*

N1—C8	1.281 (2)	O1—C1	1.432 (2)
N1—N2	1.391 (1)	O2—C9	1.231 (1)
N2—C9	1.349 (1)	C5—C8	1.466 (1)
O1—C2	1.370 (1)	C9—C10	1.509 (2)
C8—N1—N2	113.59 (9)	O2—C9—C10	121.3 (1)
C9—N2—N1	119.45 (9)	N2—C9—C10	114.27 (9)
O2—C9—N2	124.4 (1)		
C8—N1—N2—C9	176.5 (1)	N1—N2—C9—O2	5.0 (2)
N2—N1—C8—C5	−175.9 (1)	N1—N2—C9—C10	−172.2 (1)

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

D—H···A	D—H	H···A	D···A	D—H···A
O1W—H1W1···N3	0.90 (2)	1.92 (2)	2.820 (2)	179 (2)
N2—H1N2···O1W^i	0.92 (2)	2.04 (2)	2.945 (1)	171 (1)
O1W—H2W1···O2^{ii}	0.88 (2)	2.00 (2)	2.886 (2)	177 (2)

Symmetry codes: (i) $x, -\frac{1}{2} - y, z - \frac{1}{4}$; (ii) $1 - x, -y, 2 - z$.

The data collection covered a hemisphere of reciprocal space by a combination of three sets of exposures; each set had a different φ angle (0, 88 and 180°) for the crystal and each exposure of 10 s covered 0.3° in ω. 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.

Data collection: *SMART* (Siemens, 1996). Cell refinement: *SAINT* (Siemens, 1996). Data reduction: *SAINT*. Program(s) used to solve structure: *SHELXTL* (Sheldrick, 1997). Program(s) used to refine structure: *SHELXTL*. Molecular graphics: *SHELXTL*. Software used to prepare material for publication: *SHELXTL* and *PARST* (Nardelli, 1995).

References

Altomare, A., Cascarano, G., Giacovazzo, C., Guagliardi, A., Burla, M. C., Polidori, G. & Camalli, M. (1994). *J. Appl. Cryst.* **27**, 435–436.

Domiano, P., Nardelli, M., Balsamo, A., Macchia, B. & Macchia, F. (1979). *Acta Cryst.* B**35**, 1363–1372.

Fun, H.-K., Sivakumar, K., Lu, Z.-L., Duan, C.-Y., Tian, Y.-P. & You, X.-Z. (1996) *Acta Cryst.* C**52**, 986–988.

Lu, Z.-L., Duan, C.-Y., Tian, Y.-P., You, X.-Z., Fun, H.-K. & Sivakumar, K. (1996). *Acta Cryst.* C**52**, 1507–1509.

Lu, Z.-L., Shan, B.-Z., Duan, C.-Y., Tian, Y.-P., You, X.-Z., Fun, H.-K. & Sivakumar, K. (1996). *Acta Cryst.* C**52**, 1720–1722.

Ma, Y. X., Lu, Z. L., Song, Q. B. & Wu, X. L. (1994). *J. Coord. Chem.* **32**, 353–359.

Nardelli, M. (1995). *J. Appl. Cryst.* **28**, 659.

Sheldrick, G. M. (1997). *SHELXTL Software Reference Manual.* Version 5.1. Bruker AXS Inc., Madison, Wisconsin, USA.

2-Acetyl-6-phenyl-5,6,7,8-tetrahydro-1-naphthyl *p*-toluenesulfonate

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Abstract

In the title compound, $C_{25}H_{24}O_4S$, the S atom is in a distorted tetrahedral geometry. The cyclohexene ring in the structure adopts the sofa conformation. The acetyl group is twisted from the benzene ring by 37.4 (5)°. The equatorially attached phenyl ring forms a dihedral angle of 68.1 (2)° with the cyclohexene ring.

Comment

Naphthalene derivatives are widely used as intermediates in the synthesis of several polycyclic phenols which are useful as antifibrillatory agents, disinfectants and water softeners (Hauck *et al.*, 1977). β-Keto derivatives of naphthalene serve as useful synthetic intermediates in the synthesis of the subunits of daunomycinone and adiramycin, which are important anticancer drugs (Crouse *et al.*, 1981). The structure determination of the title compound, (I), was carried out in order to elucidate its molecular conformation.

(I)
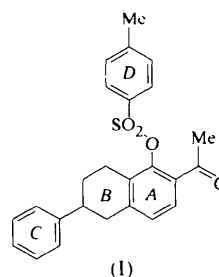
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The S atom is in a distorted tetrahedral geometry, with the maximum and minimum bond angles subtended at this atom being 120.7 (2) and 102.1 (1)°, respectively. The S1—O4 and O2—C1 bonds are almost eclipsed [torsion angle 5.6 (3)°]. The S—O, C—O and C—C distances in the structure agree with the reported mean values (Allen *et al.*, 1987). The C2—C11 distance of 1.494 (5) Å is slightly longer than the reported mean value for a unconjugated Csp^2—Csp^2 distance (1.484 Å; Allen *et al.*, 1987).

The cyclohexene ring (B) in the structure adopts an envelope conformation with the asymmetry parameter ΔC_s(C6) = 0.025 (2) (Nardelli, 1983); C6 deviates from the mean plane through the other five atoms of ring B by −0.604 (5) Å. The mean plane through ring B forms dihedral angles of 11.2 (2) and 68.1 (2)° with the planes through the adjacent benzene and the equatorially attached phenyl ring, respectively. The acetyl group is twisted out of the benzene ring (A), with an average torsion angle of 37.4 (5)° around the C2—C11 bond.

The bridging oxygen, O2, is involved in a C12—H12C···O2 intramolecular hydrogen bond. In the solid state, the inversion-related molecules exist as weak C7—H7A···O3(2 − x, 1 − y, −z) hydrogen-bonded dimers (Table 2). Along the a direction, rings A and D(x + 1, y, z) are stacked at a perpendicular distance of 3.352 (5) Å; the shortest contact observed in these two rings is 3.452 (5) Å between C3 and C24(x + 1, y, z). The possibility of π–π stacking interactions between these rings is reduced as they make a dihedral angle of 30.5°.
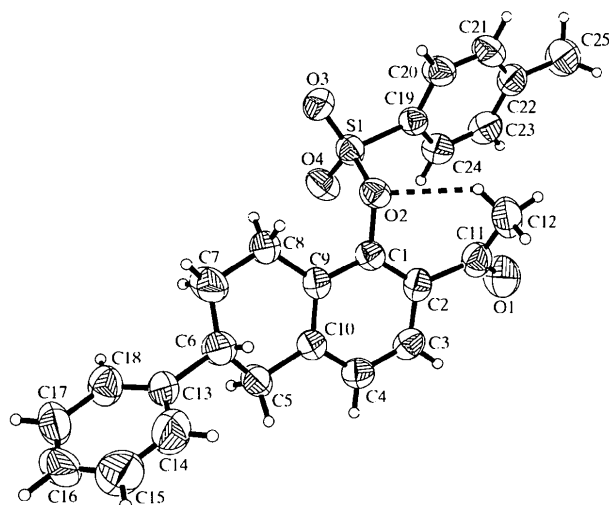

Fig. 1. The structure of (I), showing 50% probability displacement ellipsoids and the atom-numbering scheme. H atoms are displayed as small circles of arbitrary radii; one of the H atoms of C25 is hidden.

Experimental

5,8-Dihydronaphthyl acetate was prepared by acylation of 5,8-dihydronaphthol using acetyl chloride and pyridine in dry benzene. The reaction of 5,8-dihydronaphthyl acetate (1 g, 6.84 mmol) with AlCl₃ (6 g, 0.045 mmol) in dry benzene (50 ml) under reflux conditions furnished two regioisomeric arylated products in good yields which were identified as 2-acetyl-6-phenyl-5,6,7,8-tetrahydronaphthalen-1-ol and 4-acetyl-6-phenyl-5,6,7,8-tetrahydronaphthalen-1-ol. The title compound, (I), was prepared by treating the former (0.26 g, 1 mmol) with p-toluenesulfonyl chloride (0.19 g, 1 mmol) in dry benzene using pyridine as a base. Single crystals were obtained by slow evaporation of a solution of the title compound in methanol.

Crystal data

$C_{25}H_{24}O_4S$	Mo $K\alpha$ radiation
$M_r = 420.50$	$\lambda = 0.71073$ Å
Triclinic	Cell parameters from 3961
$P\bar{1}$	reflections
$a = 7.9607 (2)$ Å	$\theta = 1.45–28.30°$
$b = 9.9649 (2)$ Å	$\mu = 0.180$ mm^{-1}
$c = 14.2553 (3)$ Å	$T = 293 (2)$ K
$\alpha = 86.208 (1)°$	Needle
$\beta = 79.818 (1)°$	0.28 × 0.16 × 0.10 mm
$\gamma = 73.889 (1)°$	Colourless
$V = 1069.14 (4)$ Å^3	
$Z = 2$	
$D_x = 1.306$ Mg m^{-3}	
D_m not measured	

Data collection

Siemens SMART CCD area-detector diffractometer	2670 reflections with $I > 2\sigma(I)$
ω scans	$R_{int} = 0.043$
Absorption correction:	$\theta_{max} = 27.5°$
multi-scan (*SADABS*;	$h = -10 \rightarrow 10$
Sheldrick, 1996)	$k = -12 \rightarrow 12$
$T_{min} = 0.951$, $T_{max} = 0.982$	$l = 0 \rightarrow 18$
6628 measured reflections	
4414 independent reflections	

Refinement

Refinement on F^2	$\Delta\rho_{max} = 0.74$ e Å^{-3}
$R[F^2 > 2\sigma(F^2)] = 0.070$	$\Delta\rho_{min} = -0.42$ e Å^{-3}
$wR(F^2) = 0.195$	Extinction correction:
$S = 1.014$	*SHELXTL* (Sheldrick,
4414 reflections	1997)
274 parameters	Extinction coefficient:
H atoms: see below	0.003 (4)
$w = 1/[\sigma^2(F_o^2) + (0.0853P)^2 + 0.2795P]$	Scattering factors from *International Tables for Crystallography* (Vol. C)
where $P = (F_o^2 + 2F_c^2)/3$	
$(\Delta/\sigma)_{max} < 0.001$	

Table 1. *Selected geometric parameters (Å, °)*

S1—O2	1.617 (2)	S1—C19	1.741 (3)
S1—O3	1.424 (2)	O1—C11	1.215 (4)
S1—O4	1.421 (2)	O2—C1	1.421 (4)
O2—S1—O3	105.2 (1)	O3—S1—C19	109.2 (2)
O2—S1—O4	107.8 (1)	O4—S1—C19	110.2 (2)
O3—S1—O4	120.7 (2)	C1—O2—S1	119.2 (2)
O2—S1—C19	102.1 (1)		

O4—S1—O2—C1	5.6 (3)	C6—C5—C10—C9	−20.4 (5)
C10—C5—C6—C7	49.4 (5)	C3—C2—C11—O1	36.5 (5)
C5—C6—C7—C8	−55.1 (5)	C1—C2—C11—C12	38.2 (5)
C6—C7—C8—C9	29.4 (5)	O3—S1—C19—C20	23.4 (3)
C7—C8—C9—C10	1.3 (5)	O4—S1—C19—C24	−22.9 (3)
C8—C9—C10—C5	−4.3 (5)		

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

D—H···A	D—H	H···A	D···A	D—H···A
C12—H12C···O2	0.96	2.28	2.987 (5)	130
C7—H7A···O3ⁱ	0.97	2.47	3.238 (6)	136

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

Due to the low r/p ratio of 9.7 for observed reflections, all the H atoms were geometrically fixed and allowed to ride on the atoms to which they were attached. Rotating-group refinement was used for the methyl groups. The reflections $\overline{4}13$, 400, 523 and 107 were suppressed during refinement as they showed very poor agreement between F_o^2 and F_c^2. At the end of the refinement, a distinct peak of 0.74 e Å^{-3} at 1.02 Å from C6 suggested the possibility of a conformational disorder for the cyclohexene ring. But the refinement based on a disorder model resulted in extreme displacement parameters for the minor component (0.2 occupancy) of C6 and unrealistic bond lengths and angles involving the same. Hence, the disorder model was abandoned.

Data collection: *SMART* (Siemens, 1996). Cell refinement: *SAINT* (Siemens, 1996). Data reduction: *SAINT*. Program(s) used to solve structure: *SHELXTL* (Sheldrick, 1997). Program(s) used to refine structure: *SHELXTL*. Molecular graphics: *SHELXTL*. Software used to prepare material for publication: *SHELXTL*, *PARST* (Nardelli, 1995) and *PLATON* (Spek, 1990).

References

Allen, F. H., Kennard, O., Watson, D. G., Brammer, L., Orpen, A. G. & Taylor, R. (1987). *J. Chem. Soc. Perkin Trans.* 2, pp. S1–19.
Crouse, D. J., Hurlbut, S. L. & Wheeler, D. M. S. (1981). *J. Org. Chem.* **46**, 374–378.
Hauck, F. P., Cimarusti, C. M. & Sundeen, J. E. (1977). *Chem. Abstr.* **86**, 43447u.
Nardelli, M. (1983). *Acta Cryst.* C39, 1141–1142.
Nardelli, M. (1995). *J. Appl. Cryst.* **28**, 659.
Sheldrick, G.M. (1996). *SADABS. Program for Absorption Correction.* University of Göttingen, Germany.
Sheldrick, G. M. (1997). *SHELXTL. Structure Determination Software Programs.* Version 5.10. Bruker Analytical X-ray Systems Inc., Madison, Wisconsin, USA.
Siemens (1996). *SMART* and *SAINT. Area Detector Control and Integration Software.* Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
Spek, A. L. (1990). *Acta Cryst.* A46, C-34.

9-Hydroxy-8-iodo-4-methyl-7,8,9,10-tetrahydrobenzo[h]coumarin

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Abstract

In the title molecule, $C_{14}H_{13}IO_3$, the coumarin ring system is planar and the fused cyclohexane ring adopts a half-chair conformation. The planes of the coumarin and cyclohexane rings form a dihedral angle of 8.5 (1)°. In the crystal, the hydroxyl group and the carbonyl O atom are involved in an O—H···O intermolecular hydrogen bond. The molecules are stacked at a perpendicular distance of 3.588 (8) Å along the *a* axis.

Comment

Coumarin derivatives are found in many natural products displaying diverse biological properties. They are found to exhibit antifungal and anticoagulant properties (Parrish *et al.*, 1974). The amino and hydroxy coumarin derivatives are widely used in dye lasers (Maeda, 1984). The structural study of the title compound, (I), one of the coumarin derivatives, was performed as part of our study on coumarin derivatives.

(I)
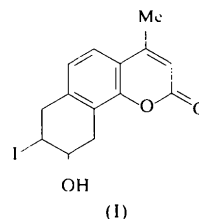
As observed in other coumarin derivatives, the C3—C4 and C5—C6 bonds in the coumarin moiety show double-bond character, and steric interactions cause the widening of angles C3—C2—O11 and C4—C10—C5, and the narrowing of angles O1—C2—O11 and O1—C9—C8 from 120° (Chinnakali *et al.*, 1997*a,b*; Kumar *et al.*, 1997). The coumarin ring system is planar, with the O11 atom deviating by a maximum