4-[1-(Phenylsulfonyl)indol-3-yl]-3a,4,-5,9b-tetrahydro-3H-cyclopenta[c]-quinoline

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In the title compound, $C_{26}H_{22}N_2O_2S$, the tetrahydropyridine ring has a conformation intermediate between half-chair and sofa. The tetrahydroquinoline mean plane makes a dihedral angle of 73.3 (1)° with the cyclopentene ring, which adopts an envelope conformation, and an angle of 45.45 (4)° with the indole best plane. The dihedral angle between the benzene and pyrrole rings is 2.6 (1)°. The orientations of the phenyl ring on the sulfonyl group and of the indole are governed by weak C—H···O interactions. The packing of the molecule in the solid state is stabilized by C—H···O and C—H···N hydrogen bonds.

Comment

Quinolines and indoles have been of interest for many years, since a large number of natural products contain these heterocyclic nuclei, and they are found in numerous commercial products including pharmaceuticals, fragrances and dyes (Padwa *et al.*, 1999). Tetrahydroquinoline derivatives
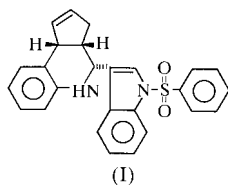

(I)

exhibit antitumour activities (Jaton *et al.*, 1997) and also act as potent antipsychotic agents (Norman *et al.*, 1996), and a compound containing the tetrahydroquinoline moiety acts as an antischistosomal drug (Billings & Heidelberger, 1982). They also possess anti-inflammatory (Ohnishi *et al.*, 1981), antiamœbic (Bailey *et al.*, 1979), antiulcer (Uchida *et al.*, 1989) and analgesic (Shaaban *et al.*, 1977) activities. In order to obtain detailed information on molecular conformation, the X-ray structure determination of the title compound, (I), has been carried out and the results are presented here.

The total puckering amplitude (Cremer & Pople, 1975) of the tetrahydropyridine ring, *B*, is $Q_T = 0.450$ (2) Å and the values of the lowest displacement asymmetry parameters (Nardelli, 1983*a*), Δ_2(C6—C1) = 0.053 (1) and Δ_S(C12) = 0.060 (1), are indicative of a conformation intermediate between half-chair and sofa. The total puckering amplitude of the cyclopentene ring, *A*, is $Q_T = 0.276$ (3) Å and the value Δ_S(C11) = 0.004 (2) of the lowest asymmetry parameter is indicative of an envelope conformation. The C7—C11—C12—C13 torsion angle of 175.1 (2)° is indicative of the way the indole substituent is bonded to the tetrahydroquinoline.

The indole system is not strictly planar, the dihedral angle formed by the benzo and pyrrole planes being 2.6 (1)°. Atom N15 deviates by 0.148 (2) Å from the mean plane passing through C14, C16 and S22. This slight pyramidalization behaviour is also observed in related indoles (Yokum & Fronczek, 1997; Beddoes *et al.*, 1986). The torsion angles O23—S22—N15—C16 = 171.2 (2) and O23—S22—C25—C26 = 43.2 (2)° describe the conformation of the phenylsulfonyl group with respect to the indole system, which causes the best planes of the indole and phenyl rings to form a dihedral angle of 85.6 (1)°, as observed in similar structures (Yokum & Fronczek, 1997).

In the indole system, the endocyclic angles at C17 and C20 are contracted to 116.7 (2) and 118.5 (2)°, respectively, while those at C16 and C19 are expanded to 122.6 (2) and 121.2 (2)°, respectively. This would appear to be a real effect caused by the fusion of the smaller pyrrole ring to the six-membered benzene ring and the strain is taken up by angular distortion rather than by bond length distortions. A similar effect has also been observed by Govindasamy *et al.* (1999) and Sivaraman *et al.* (1994, 1996). The bond distances S22=O24 = 1.432 (2), S22=O23 = 1.429 (2) and S22—C25 = 1.758 (2) Å are comparable with the reported values [S=O = 1.435 (5) and S—C = 1.767 (7) Å; Govindasamy *et al.*, 1998], whereas S22—N15 = 1.659 (2) Å varies appreciably from the reported value of 1.685 (5) Å.
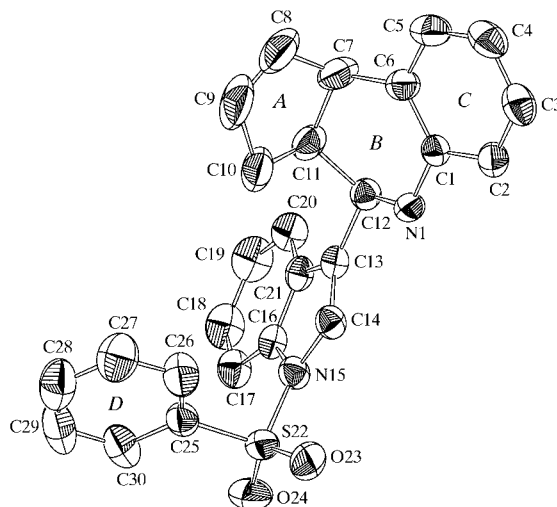

Figure 1
The molecular structure of (I) showing 50% probability displacement ellipsoids and the atom-numbering scheme. H atoms have been omitted for clarity.

The orientation of the phenyl ring, *D*, is conditioned by the weak C30—H30···O24 interaction, while the orientation of the indole substituent is influenced by the weak interaction C17—H17···O24 (Table 2). The torsion angles O24—S22—C25—C30 = −1.3 (2), N15—S22—C25—C30 = 113.3 (2), O24—S22—N15—C16 = 41.3 (2) and S22—N15—C16—C17 = −18.2 (3)° quantitatively define these orientations.

Apart from the normal van der Waals interactions, the packing of the molecule in the solid state is stabilized by C—H···O and C—H···N intermolecular hydrogen bonds (Table 2).

Experimental

To a solution of 4-phenylsulfonyl-3-(*N*-phenylformimidoyl)indole (0.648 g, 0.018 mol) and cyclopentadiene (0.237 g, 0.036 mol) in acetonitrile (10 ml) protected by a guard tube was added indium trichloride (0.081 g, 20 mol%) and the mixture was stirred at room temperature for 30 min. Water (20 ml) was added to the reaction mixture, which was then extracted with chloroform (3 × 10 ml), washed with brine (10 ml), dried over anhydrous sodium sulfate and concentrated under reduced pressure. The crude product was purified by column chromotography using silica gel (60–120 mesh) and eluted with petroleum ether–ethyl acetate (90:10) to afford compound (I) (yield 83%).

Crystal data

$C_{26}H_{22}N_2O_2S$	$D_x = 1.264$ Mg m^{-3}
$M_r = 426.52$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/n$	Cell parameters from 8192
$a = 11.4515$ (2) Å	reflections
$b = 8.6572$ (1) Å	$\theta = 1.45$–$28.33°$
$c = 22.6109$ (4) Å	$\mu = 0.169$ mm^{-1}
$\beta = 90.864$ (1)°	$T = 293$ (2) K
$V = 2241.34$ (6) Å^3	Block, pale yellow
$Z = 4$	$0.48 \times 0.34 \times 0.28$ mm

Data collection

Siemens SMART CCD area-detector diffractometer	$R_{int} = 0.040$
	$\theta_{max} = 28.28°$
ω scans	$h = -9 \rightarrow 15$
14 562 measured reflections	$k = -11 \rightarrow 10$
5435 independent reflections	$l = -29 \rightarrow 29$
3542 reflections with $I > 2\sigma(I)$	Intensity decay: <2%

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0586P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.054$	$+ 0.9637P]$
$wR(F^2) = 0.149$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.019$	$(\Delta/\sigma)_{max} = 0.003$
5435 reflections	$\Delta\rho_{max} = 0.50$ e Å^{-3}
280 parameters	$\Delta\rho_{min} = -0.49$ e Å^{-3}
H-atom parameters constrained	

Table 1
Selected geometric parameters (Å, °).

S22—O23	1.429 (2)	S22—O24	1.432 (2)
O23—S22—O24	120.9 (1)	N15—S22—C25	105.5 (1)
O23—S22—N15	105.3 (1)	C16—N15—C14	107.6 (2)
O24—S22—N15	107.1 (1)	C16—N15—S22	126.8 (1)
O23—S22—C25	108.2 (1)	C14—N15—S22	122.7 (2)
O24—S22—C25	108.9 (1)		
C1—N1—C12—C13	−171.4 (2)	N15—S22—C25—C26	−69.0 (2)
C7—C11—C12—C13	175.1 (2)		

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

D—H···A	D—H	H···A	D···A	D—H···A
C17—H17···O24	0.93	2.51	3.074 (3)	119
C30—H30···O24	0.93	2.54	2.912 (3)	104
C29—H29···O23^i	0.93	2.66	3.568 (4)	166
C2—H2···O23^{ii}	0.93	2.61	3.323 (3)	134
C19—H19···N1^{iii}	0.93	2.71	3.602 (3)	162

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

Data collection: *SMART* (Siemens, 1996); cell refinement: *SAINT* (Siemens, 1996); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ZORTEP* (Zsolnai, 1997); software used to prepare material for publication: *SHELXL*97 and *PARST* (Nardelli, 1983*b*, 1995).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: NA1443). Services for accessing these data are described at the back of the journal.

References

Bailey, D. M., Mount, E. M., Siggins, J., Carlson, J. A., Yarinsky, A. & Slighter, R. G. (1979). *J. Med. Chem.* **22**, 599–601.
Beddoes, R. L., Dalton, L., Joule, J. A., Mills, O. S., Street, J. D. & Watt, C. I. F. (1986). *J. Chem. Soc. Perkin Trans.* 2, pp. 787–797.
Billings, P. C. & Heidelberger, C. (1982). *Cancer Res.* **42**, 2692–2696.
Cremer, D. & Pople, J. A. (1975). *J. Am. Chem. Soc.* **97**, 1354–1358.
Govindasamy, L., Velmurugan, D., Ravikumar, K. & Mohanakrishnan, A. K. (1998). *Acta Cryst.* C**54**, 635–637.
Govindasamy, L., Velmurugan, D., Shanmuga Sundara Raj, S. & Fun, H.-K. (1999). *Acta Cryst.* C**55**, 1315–1317.
Jaton, J. C., Roulin, K., Rose, K., Sirotnak, F. M., Lewenstein, A., Brunner, G., Fankhauser, C. P. & Burger, U. (1997). *J. Nat. Prod.* **60**, 356–360.
Nardelli, M. (1983*a*). *Acta Cryst.* C**39**, 1141–1142.
Nardelli, M. (1983*b*). *Comput. Chem.* **7**, 95–98.
Nardelli, M. (1995). *J. Appl. Cryst.* **28**, 659.
Norman, M. H., Navas, F., Thompson, J. B. & Rigdon, G. C. (1996). *J. Med. Chem.* **39**, 4692–4703.
Ohnishi, H., Kosuzume, H., Yamaguchi, K., Ohkura, M., Satoh, M., Uohama, M., Toyonaka, Y. & Suzuki, Y. (1981). *Jpn J. Pharmacol.* **31**, 747–756.
Padwa, A., Brodney, M. A., Liu, B., Satake, K. & Wu, T. (1999). *J. Org. Chem.* **64**, 3595–3607.
Shaaban, M. A., Ghoneim, K. M. & Khalifa, M. (1977). *Pharmazie*, **32**, 90–92.
Sheldrick, G. M. (1997). *SHELXS*97 and *SHELXL*97. University of Göttingen, Germany.
Siemens (1996). *SMART* and *SAINT*. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
Sivaraman, J., Subramanian, K., Velmurugan, D. & Subramanian, E. (1994). *Acta Cryst.* C**50**, 787–789, 789–791.
Sivaraman, J., Subramanian, K., Velmurugan, D., Subramanian, E. & Seetharaman, J. (1996). *J. Mol. Struct.* **385**, 123–128.
Uchida, M., Chihiro, M., Morita, S., Kanbe, T., Yamashita, H., Yamasaki, K., Yabuuchi, Y. & Nakagawa, K. (1989). *Chem. Pharm. Bull. (Tokyo)*, **37**, 2109–2116.
Yokum, S. T. & Fronczek, F. R. (1997). *Acta Cryst.* C**53**, 362–363.
Zsolnai, L. (1997). *ZORTEP*. University of Heidelberg, Germany.