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4-Benzyl-2,9-bis(phenylsulfonyl)-1,2,3,4-tetrahydro-9*H*-β-carboline

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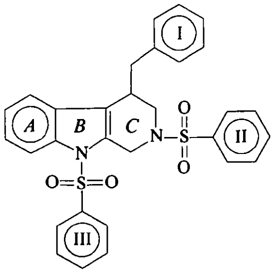
Abstract

In the title compound, $C_{30}H_{26}N_2O_4S_2$, the six-membered aromatic and five-membered heterocyclic rings are planar, and the six-membered heterocyclic ring is in a half-chair conformation. The phenylsulfonyl group attached to the N atom of the five-membered ring is almost perpendicular to the β-carboline moiety. The phenylsulfonyl groups attached to N2 and N1 are in equatorial positions. The molecules are stabilized by weak inter- and intramolecular hydrogen bonds.

Comment

The tetrahydro-β-carboline moiety occurs in many indole alkaloids and the assignment of stereochemistry to these systems is often crucial in the structure elucidation of natural products of this type (Everett *et al.*, 1990). Some β-carboline (9*H*-pyrido[3,4-*b*]indole) derivatives have been shown to be antagonists of benzodiazepines (Oakley & Jones, 1980) and have aroused considerable interest in neuropharmacology (Braestrup *et al.*, 1980; Ninan *et al.*, 1982). The structural studies of some β-carboline derivatives have been instrumental in the development of the inverse agonist/agonist pharmacophore of the benzodiazepine receptor (BzR) site. The BzR is located in the GABA receptor ion channel and plays an important role in the molecular mechanisms controlling anxiety, convulsions, memory learning and sleep in animals (Cox & Cook, 1995).

A *ZORTEP* diagram (Zsolnai, 1997) of the title molecule, (1), with the atomic numbering scheme is shown in Fig. 1. The geometries around the S atoms (S1 and S2) are distorted from ideal tetrahedral, with the largest deviations in the O—S—O [O2—S1—O1 119.9 (3) and O4—S2—O3 120.8 (3)°] and O—S—N angles [O2—S1—N1 106.3 (2), O1—S1—N1 106.9 (3), O4—S2—N2 106.3 (2) and O3—S2—N2 107.4 (3)°], but the geometries do conform to the non-tetrahedral arrangement commonly observed in dibenzenesulfonamides (Cotton & Stokely, 1970). The values of the C—N distances in ring *C* [N2—C8 1.476 (7) and N2—C7 1.489 (7) Å] are larger than those in ring *B* [N1—C5 1.438 (7) and N1—C6 1.438 (6) Å]. The S—N bond distances [S1—N1 1.670 (5) and S2—N2 1.638 (4) Å] lie in the range 1.63–1.69 Å given by Kálmán *et al.* (1981). The average S—O, S—C and S—N distances of 1.435, 1.772 and 1.654 Å, respectively, are comparable with those found in *N*-phenylsulfonamides (Gomes *et al.*, 1993).



(1)

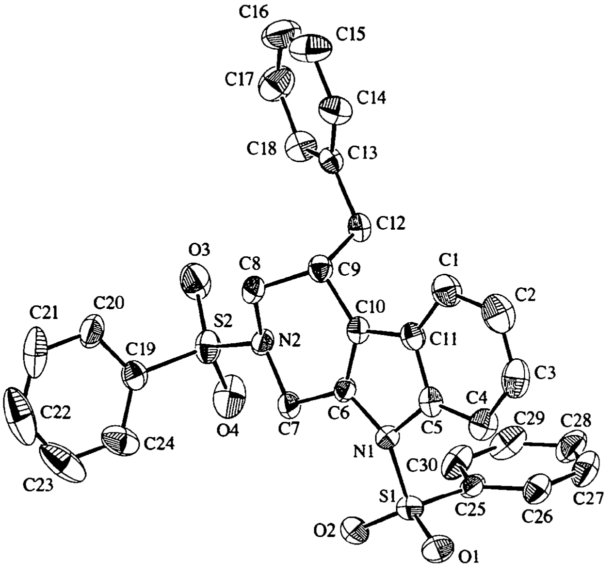


Fig. 1. The structure of (1) showing 30% probability displacement ellipsoids with the atomic numbering scheme.

The three phenyl rings (I, II and III) are planar. The plane through ring III makes an angle of 99.0 (2)° with the plane of the β-carboline moiety. Rings II and I are inclined with respect to the β-carboline moiety by 67.5 (2) and 26.4 (2)°, respectively. Phenyl ring I is nearly perpendicular to phenyl rings II and III [dihedral angles 93.0 (2) and 87.5 (2)°, respectively]. The phenylsulfonyl groups attached to N2 and N1 are in equatorial positions [S2—N2—C7—C6 172.6 (4) and S2—N2—C8—C9 −150.9 (4)°] and phenyl ring I bonded to C9 is in an axial position [N2—C8—C9—C12 73.2 (6) and C12—C9—C10—C6 −102.3 (6)°].

In the β-carboline moiety, rings *A* and *B* are planar, and the six-membered heterocyclic ring *C* is in a half-chair conformation (with atom C8 −0.388 Å above and atom N2 0.203 Å below the least-squares plane defined by the six ring atoms). At the *A*/*B* ring junction, the torsion angles are C4—C5—C11—C1 −1.5 (9) and N1—C5—C11—C10 −1.0 (6)°, and at the *B*/*C* junction, N1—C6—C10—C11 1.8 (6) and C7—C6—C10—C9 −2.3 (9)°. The angles between the best planes of the rings are *A*/*B* 1.3 (2), *B*/*C* 7.2 (2) and *C*/*A* 6.2 (2)°. The molecules are stabilized by C—H···O-type intermolecular hydrogen bonds. Intramolecular C—H···O-type bonding is present and stablizes the system in the solid state.

Experimental

The title compound was synthesized by the reductive condensation process (Mohanakrishnan & Srinivasan, 1996) in the Department of Organic Chemistry, University of Madras, India. Good quality crystals were obtained from acetone solution at room temperature.

Crystal data

$C_{30}H_{26}N_2O_4S_2$
$M_r = 542.65$
Triclinic
$P\bar{1}$
$a = 10.184\,(1)$ Å
$b = 10.941\,(1)$ Å
$c = 13.441\,(1)$ Å
$\alpha = 84.80\,(2)°$
$\beta = 67.94\,(2)°$
$\gamma = 82.65\,(2)°$
$V = 1375.1\,(2)$ Å^3
$Z = 2$
$D_x = 1.311$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 8$–$20°$
$\mu = 0.232$ mm^{-1}
$T = 293\,(2)$ K
Transparent rectangular
0.60 × 0.55 × 0.50 mm
Pale yellow

Data collection

Siemens *R*3*m*/*V* diffractometer
$\omega/2\theta$ scans
Absorption correction: none
3870 measured reflections
3618 independent reflections
2018 reflections with $I > 2\sigma(I)$

$R_{\rm int} = 0.044$
$\theta_{\max} = 22.55°$
$h = 0 \rightarrow 10$
$k = -11 \rightarrow 11$
$l = -13 \rightarrow 14$
2 standard reflections
frequency: 60 min
intensity decay: <1%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.061$
$wR(F^2) = 0.192$
$S = 0.963$
3613 reflections
344 parameters
H atoms riding
$w = 1/[\sigma^2(F_o^2) + (0.1P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$

$\Delta\rho_{\max} = 0.272$ e Å^{-3}
$\Delta\rho_{\min} = -0.219$ e Å^{-3}
Extinction correction: *SHELXL*93
Extinction coefficient: 0.005 (2)
Scattering factors from *International Tables for Crystallography* (Vol. C)

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

S1—O2	1.426 (4)	S2—N2	1.638 (4)
S1—O1	1.446 (4)	S2—C19	1.786 (6)
S1—N1	1.670 (5)	N1—C5	1.438 (7)
S1—C25	1.758 (6)	N1—C6	1.438 (6)
S2—O4	1.423 (5)	N2—C8	1.476 (7)
S2—O3	1.443 (5)	N2—C7	1.489 (7)
O2—S1—O1	119.9 (3)	C6—N1—S1	124.7 (4)
O2—S1—N1	106.3 (2)	C8—N2—C7	116.1 (4)
O1—S1—N1	106.9 (3)	C8—N2—S2	116.8 (3)
O2—S1—C25	109.2 (3)	C7—N2—S2	116.3 (3)
O1—S1—C25	109.1 (3)	C11—C5—N1	107.6 (5)
N1—S1—C25	104.3 (2)	C4—C5—N1	129.6 (6)
O4—S2—O3	120.8 (3)	C10—C6—N1	110.2 (5)
O4—S2—N2	106.3 (2)	N1—C6—C7	124.9 (5)
O3—S2—N2	107.4 (3)	N2—C7—C6	107.5 (4)
O4—S2—C19	107.2 (3)	C24—C19—S2	120.3 (6)
O3—S2—C19	107.5 (3)	C20—C19—S2	119.3 (5)
N2—S2—C19	106.8 (2)	C30—C25—S1	120.8 (5)
C5—N1—C6	106.2 (4)	C26—C25—S1	119.3 (5)
C5—N1—S1	121.7 (4)		
O2—S1—N1—C5	178.1 (4)	S2—N2—C8—C9	−150.9 (4)
O1—S1—N1—C5	48.9 (5)	N2—C8—C9—C10	−48.8 (6)
C25—S1—N1—C5	−66.6 (5)	N2—C8—C9—C12	73.2 (6)
O2—S1—N1—C6	−36.1 (5)	N1—C6—C10—C11	1.8 (6)
O1—S1—N1—C6	−165.2 (4)	N1—C6—C10—C9	−177.2 (4)
C25—S1—N1—C6	79.3 (5)	C7—C6—C10—C9	−2.3 (9)

O4—S2—N2—C8	175.6 (4)	C12—C9—C10—C6	−102.3 (6)
O3—S2—N2—C8	45.0 (5)	C4—C5—C11—C1	−1.5 (9)
C19—S2—N2—C8	−70.1 (4)	N1—C5—C11—C1	178.6 (5)
O4—S2—N2—C7	−41.5 (5)	N1—C5—C11—C10	−1.0 (6)
O3—S2—N2—C7	−172.1 (4)	O4—S2—C19—C24	20.2 (6)
C19—S2—N2—C7	72.8 (4)	O3—S2—C19—C24	151.5 (5)
C3—C4—C5—N1	−179.5 (6)	N2—S2—C19—C24	−93.5 (5)
C6—N1—C5—C11	2.1 (6)	O4—S2—C19—C20	−159.7 (5)
S1—N1—C5—C11	153.4 (4)	O3—S2—C19—C20	−28.4 (5)
C6—N1—C5—C4	−177.8 (5)	N2—S2—C19—C20	86.7 (5)
S1—N1—C5—C4	−26.5 (8)	S2—C19—C20—C21	179.7 (5)
C5—N1—C6—C10	−2.5 (6)	S2—C19—C24—C23	−178.5 (5)
S1—N1—C6—C10	−152.6 (4)	O2—S1—C25—C30	29.9 (6)
C5—N1—C6—C7	−177.3 (5)	O1—S1—C25—C30	162.7 (5)
S1—N1—C6—C7	32.5 (7)	N1—S1—C25—C30	−83.4 (5)
C8—N2—C7—C6	−44.2 (6)	O2—S1—C25—C26	−153.5 (4)
S2—N2—C7—C6	172.6 (4)	O1—S1—C25—C26	−20.8 (5)
C10—C6—C7—N2	12.0 (8)	N1—S1—C25—C26	93.2 (5)
N1—C6—C7—N2	−173.8 (5)	S1—C25—C26—C27	−177.3 (5)
C7—N2—C8—C9	66.1 (6)	S1—C25—C30—C29	177.4 (5)

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C4—H4···O1	0.93 (1)	2.42 (1)	3.01 (1)	121.0 (6)
C18—H18···O4^{i}	0.93 (1)	2.53 (1)	3.33 (1)	144.8 (6)
C29—H29···O3^{i}	0.93 (1)	2.58 (1)	3.24 (1)	128.5 (7)
C23—H23···O1^{ii}	0.93 (1)	2.56 (1)	3.45 (1)	161.1 (9)

Symmetry codes: (i) $-x, 1-y, -z$; (ii) $-x, 1-y, 1-z$.

The large discrepancy between the *R* and *wR* values is due to the high thermal vibration present in phenyl ring II (atoms C21, C22 and C23) on the β-carboline moiety. H atoms were geometrically positioned and refined using a riding model.

Data collection: *P3/P4-PC Diffractometer Program* (Siemens, 1991). Cell refinement: *P3/P4-PC Diffractometer Program*. Data reduction: *SHELXTL-Plus* (Sheldrick, 1991). Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *ZORTEP* (Zsolnai, 1997). Software used to prepare material for publication: *SHELXL93* and *PARST* (Nardelli, 1983, 1995).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: PT1051). Services for accessing these data are described at the back of the journal.

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1,3,3-Trimethylindoline-2-spiro-2′-3′-methyl-2′*H*-phenanthro[9,10-*b*][1,4]oxazine

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Abstract

In the title compound, $C_{27}H_{24}N_2O$, both benzo and phenanthro rings are essentially planar, the dihedral angle between them being 73.61 (4)°. The non-aromatic five- and six-membered rings adopt deformed envelope and half-chair conformations, respectively. Molecules are linked by weak intermolecular C—H···N interactions which exhibit C···N non-bonded contacts of 3.481 (2) and 3.540 (2) Å, respectively.

Comment

Spirooxazine is the most important member of one of the best known organic photochromic systems (Durr & Laurent, 1990). Many applications have been envisaged in several key areas such as high-density optical storage, optical switching, photochromic lenses, image processing and displays. In order to study the relationship between molecular structure and photochromic behaviour, the structures of several spirooxazines have been determined (Maeda *et al.*, 1994; Osano *et al.*, 1991; Clegg *et al.*, 1991), most of them concerning indolinespironaphthooxazines and indolinespiroquinolinooxazines. In