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2-(3-Bromo-1-phenylsulfonyl-1*H*-indol-2-ylmethylsulfanyl)-6-methyl-1*H*-benzimidazole

T. Ravishankar,[a] K. Chinnakali,[a]* N. Arumugam,[b] P. C. Srinivasan,[b] Anwar Usman[c] and Hoong-Kun Fun[c]*

[a]Department of Physics, Anna University, Chennai 600 025, India, [b]Department of Organic Chemistry, University of Madras, Guindy Campus, Chennai 600 025, India, and [c]X-ray Crystallography Unit, School of Physics, Universiti Sains Malaysia, 11800 USM, Penang, Malaysia

Correspondence e-mail: kali@annauniv.edu, hkfun@usm.my

Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.010 Å
R factor = 0.072
wR factor = 0.219
Data-to-parameter ratio = 14.5

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

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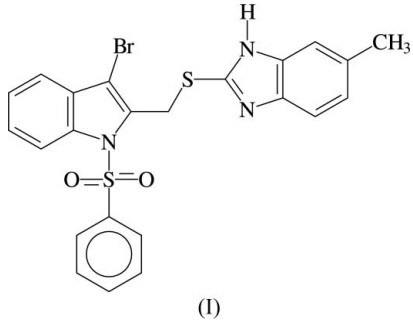
In the title compound, $C_{23}H_{18}BrN_3O_2S_2$, the sulfonyl-bound phenyl ring and benzimidazole moiety are nearly orthogonal to the indole ring system. The molecular structure is stabilized by C—H···Br and C—H···O hydrogen bonding interactions. In the crystal structure, glide-related molecules are linked by N—H···N hydrogen bonds to form chains along the *c* axis and adjacent chains are interlinked by C—H···π interactions into a three-dimensional network.

Comment

Indole and its derivatives have antibacterial, antifungal (Wang & Ng, 2002; Singh *et al.*, 2000; Tsotinis *et al.*, 1997; Quetin-Leclercq *et al.*, 1995) and antitumor activities (Andreani *et al.*, 2001; Bradlow *et al.*, 1999; Cirrincione *et al.*, 1999; Tiwari *et al.*, 1994; Dashwood *et al.*, 1994). Polyhalogenated indole derivatives exhibit marked antimicrobial activity against Gram-positive bacteria, Gram-negative bacteria and fungi (Piscopo *et al.*, 1990; Piscopo *et al.*, 1990). Certain indole derivatives are used as neuroprotectants (Stolc, 1999). Some of the indole alkaloids extracted from plants possess interesting cytotoxic, antitumor or antiparasitic properties (Quetin-Leclercq, 1994; Mukhopadhyay *et al.*, 1981). As part of our investigations of indole derivatives, we have undertaken the X-ray structure analysis of the title compound, (I).



(I)

The indole ring system in (I) (Fig. 1) is planar, with a maximum deviation of 0.027 (4) Å for atom N1. The N—Csp^2 bond lengths, *viz*. N1—C1 [1.425 (7) Å] and N1—C8 [1.408 (6) Å], are greater than the mean value of 1.355 (14) Å reported for N atoms with planar configurations (Allen *et al.*, 1987). As a result of the repulsive interaction between the short S═O bonds, atom S1 has a distorted tetrahedral configuration, with the O1—S1—O2 [120.3 (3)°] and N1—S1—C9 [104.9 (2)°] angles deviating significantly from ideal tetrahedral values. As observed in other related phenylsulfonylindoles (Ravishankar *et al.*, 2003*a*,*b*), the orientation of the phenylsulfonyl group with respect to the indole moiety [O1—S1—N1—C1 = −28.9 (5), O2—S1—N1—C8 = 44.6 (5)

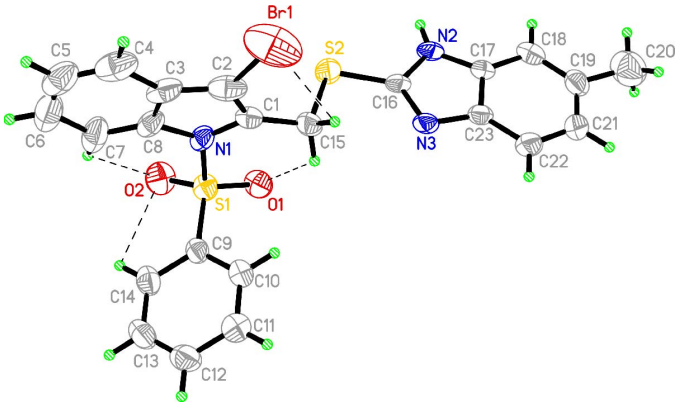


Figure 1
The structure of (I), showing the atom-numbering scheme and intramolecular hydrogen bonds (as dashed lines). Displacement ellipsoids are drawn at the 30% probability level.

and N1—S1—C9—C10 = −74.1 (5)°] is influenced by intramolecular C—H···O interactions, namely C7—H7···O2, C14—H14···O2 and C15—H15*A*···O1 (Table 1), involving the sulfonyl atoms O1 and O2. These interactions generate rings of graph-set motif *S*(5) or *S*(6) (Bernstein *et al.*, 1995; Etter, 1990). The sulfonyl-bound phenyl ring is orthogonal to the indole ring system, forming a dihedral angle of 88.5 (2)°.

The N1—C1—C15—S2 torsion angle of 83.3 (5)° describes the orientation of the methylsulfanyl benzimidazole substituent with respect to the indole ring system and the torsion angle C1—C15—S2—C16 of 169.4 (4)° shows how the benzimidazole moiety is oriented. This orientation is influenced by the intramolecular C15—H15*B*···Br1 interaction, which generates a ring of graph set motif S(5) (Fig. 1). The benzimidazole moiety is planar within 0.013 (4) Å and it forms dihedral angles of 87.7 (2) and 24.8 (2)°, respectively, with the mean planes through the indole moiety and phenyl ring of the phenylsulfonyl group.

Glide-related molecules are linked by N2—H2···N3^{i} hydrogen bonds to form a chain along the *c* axis (symmetry code as in Table 1). As seen in Fig. 2, adjacent chains are interlinked to form a three-dimensional network by C—H···π interactions (Table 1), involving the methyl H atoms H20*A* and H20*C*, the benzene ring (centroid *Cg*2) of the indole ring system and the sulfonyl-bound phenyl ring (centroid *Cg*1).

Experimental

To a solution of 3-bromo-3-bromomethyl-1-phenylsulfonylindole (4.29 g, 10 mmol), a solution of 2-mercapto-5-methylbenzimidazole (1.69 g, 10 mmol) in dimethylformamide (30 ml) was added, followed by anhydrous potassium carbonate (5 g). The resulting solution was stirred for 12 h, then poured over ice water (100 ml) and stirred for 10 min. It was then extracted with chloroform (100 ml) and the organic layer was washed twice with water (2 × 50 ml). The solvent was removed by distillation, after drying over anhydrous sodium sulfate. The residue was chromatographed on a silica-gel column (350 mesh) and eluted successively with 20%, 25% and 30% ethyl acetate in hexane. The 30% ethyl acetate eluent gave the title compound, which was then crystallized from hexane:chloroform (2:1).

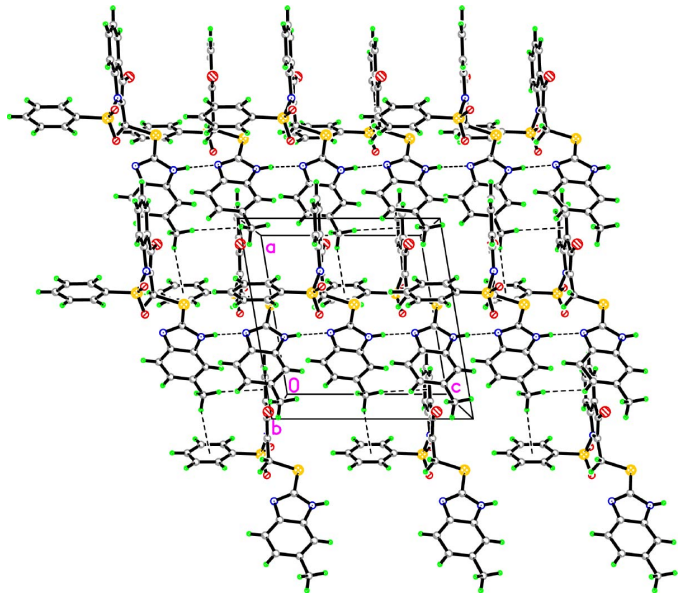


Figure 2
A view of the N—H···N and C—H···π hydrogen-bonded network in (I). All interactions are shown as dashed lines.

Crystal data

$C_{23}H_{18}BrN_3O_2S_2$
M_r = 512.43
Monoclinic, $P2_1/c$
a = 9.8818 (5) Å
b = 24.3572 (13) Å
c = 9.7867 (5) Å
β = 99.420 (1)°
V = 2323.8 (2) Å^3
Z = 4
D_x = 1.465 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 4063 reflections
θ = 2.3–28.3°
μ = 1.97 mm^{-1}
T = 293 (2) K
Block, colorless
0.50 × 0.46 × 0.40 mm

Data collection

Bruker SMART CCD area-detector diffractometer
ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
T_{min} = 0.394, T_{max} = 0.454
11 290 measured reflections
4080 independent reflections
2995 reflections with $I > 2\sigma(I)$
R_{int} = 0.022
θ_{max} = 25.0°
$h = -11 \rightarrow 11$
$k = -28 \rightarrow 21$
$l = -11 \rightarrow 11$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.072
$wR(F^2)$ = 0.219
S = 1.03
4080 reflections
281 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.1113P)^2 + 3.2827P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 1.06 e Å^{-3}
$\Delta\rho_{min}$ = −0.95 e Å^{-3}

Table 1
Hydrogen-bonding geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
C7—H7···O2	0.93	2.38	2.963 (9)	120
C14—H14···O2	0.93	2.54	2.911 (8)	104
C15—H15*A*···O1	0.97	2.24	2.836 (7)	118
C15—H15*B*···Br1	0.97	2.90	3.314 (6)	107
N2—H2···N3^{i}	0.86	1.99	2.846 (6)	172
C20—H20*A*···*Cg*1^{ii}	0.96	2.96	3.676 (10)	132
C20—H20*C*···*Cg*2^{ii}	0.96	2.79	3.726 (12)	165

Symmetry codes: (i) $x, \frac{3}{2} - y, z - \frac{1}{2}$; (ii) $1 + x, \frac{3}{2} - y, z - \frac{1}{2}$. *Cg*1 is the centroid of ring C9–C14 and *Cg*2 is the centroid of ring C3–C8.

The H atoms were positioned geometrically and treated as riding on their parent atoms, with N—H = 0.86 Å, C—H distances of 0.93 (aromatic), 0.97 (methylene) and 0.96 Å (methyl), and with U_{iso}(H) = 1.5U_{eq}(methyl C) and 1.2U_{eq}(other atoms). Owing to large displacement parameters, the U_{ij} components of C3, C4, C5, C6, C7, C8 and Br1 atoms were restrained to isotropic behavior. An unassigned maximum residual density was observed 0.71 Å from atom H21.

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 *PLATON* (Spek, 2003).

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