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2-Bromo-*N*-[3-bromo-1-(phenylsulfonyl)-indol-2-ylmethyl]-4-methylaniline

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Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.014 Å
R factor = 0.056
wR factor = 0.135
Data-to-parameter ratio = 13.3

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

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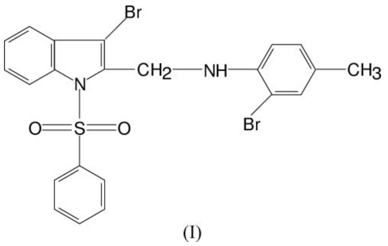
The title compound, $C_{22}H_{18}Br_2N_2O_2S$, crystallizes in the centrosymmetric space group $P\overline{1}$ with two molecules in the asymmetric unit. The two crystallographically independent molecules differ in the orientation of the aniline substituent with respect to the indole moiety. In both molecules, the S atom shows a distorted tetrahedral geometry. The molecular structure is stabilized by C—H$\cdots$O, N—H$\cdots$O, N—H$\cdots$Br and C—H$\cdots\pi$ intramolecular interactions and the molecular packing is stabilized by C—H$\cdots$Br, C—H$\cdots$O and C—H$\cdots\pi$ interactions.

Comment

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). These types of compounds are also used as anti-microbial and anti-inflammatory agents (El-Sayed *et al.*, 1986). Sulfonamide-containing drugs behave as diuretics (Crawford & Kennedy, 1959; Camerman & Camerman, 1975). Investigations using spectroscopic methods have revealed the DNA-binding activity of the indole molecule (Sivaraman *et al.*, 1996). The indole ring system is also found to occur in plants (Nigović *et al.*, 2000); for example, indole-3-acetic acid is a naturally occurring plant-growth hormone that controls several plant-growth activities (Moore, 1989; Fargasova, 1994). Against this background, and in order to obtain detailed information on its molecular conformation in the solid state, an X-ray study on the title compound, (I), was carried out.



(I)

The asymmetric unit of (I) consists of two crystallographically independent molecules, *viz*. *A* and *B*. The corresponding bond lengths and angles of *A* and *B* agree with each other, but the orientation of the aniline substituent with respect to the indole moiety in *A* is different from that in *B*. This can be seen from the N1—C8—C9—N2 and C8—C9—N2—C10 torsion angles of 95.5 (8) [−60.5 (10)° in *B*] and 176.5 (6)° [−83.2 (9)° in *B*], respectively. The geometry of molecule *A* agrees with that of a closely related molecule, namely 2-bromo-*N*-[3-bromo-*N*-(phenylsulfonyl)indol-2-ylmethyl]aniline, (II) (Govind *et al.*, 2002).

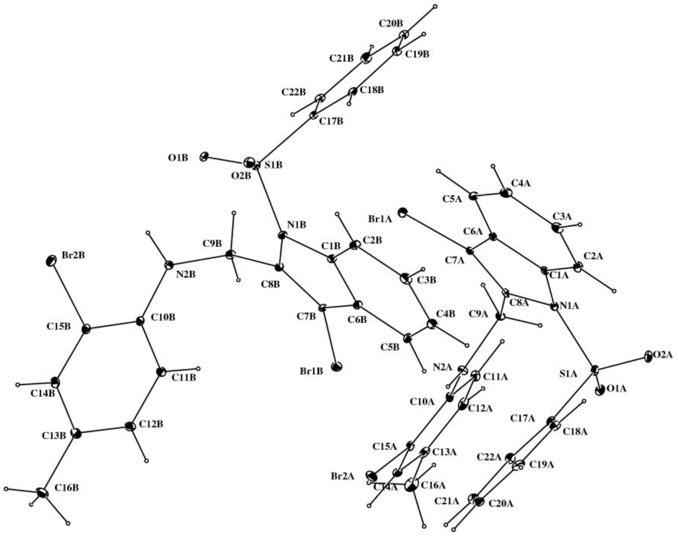


Figure 1
A view of the two crystallographically independent molecules in the asymmetric unit. Displacement ellipsoids are shown at the 30% probability level.

The torsion angles O2—S1—N1—C1 [−46.0 (6) and −48.2 (6)° in *A* and *B*] and O2—S1—C17—C22 [−156.1 (6) and −164.8 (6)°] describe the conformation of the phenylsulfonyl group with respect to the indole moiety; the mean planes through the indole moiety and the phenyl ring bound to the sulfonyl group form a dihedral angle of 84.8 (4)° in molecule *A* and 86.5 (4)° in molecule *B*. In *A*, the phenyl ring of the aniline substituent forms a dihedral angle of 84.9 (4)° with the indole moiety, while in *B* this value is 77.8 (4)°. In both molecules, the S atom is in a distorted tetrahedral configuration. As reported previously for related phenylsulfonylindole derivatives (Sankaranarayanan *et al.*, 2001; Govind *et al.*, 2002; Seshadri *et al.*, 2002), significant distortion from the ideal values is observed for O—S—O and N—S—C angles (Table 1). The relatively large values of the C—N distances in the indole moiety are due to the electron-withdrawing character of the phenylsulfonyl group. The molecular structure is stabilized by C—H···O, N—H···O, N—H···Br and C—H···π intramolecular interactions (Table 2). The observed intramolecular interactions are similar to those reported for (II) (Govind *et al.*, 2002). A short Br···Br contact of 3.500 (2) Å is observed between atoms Br2*A* and Br1*B*. The molecular packing in the crystal is stabilized by C—H···Br, C—H···O and C—H···π interactions.

Experimental

A solution of 1-phenylsulfonyl-2-bromomethyl-2-bromoindole (4.29 g, 10 mmol) and 2-bromo-4-methylaniline (2 equivalents) in dry DMF (25 ml) containing finely powdered K_2CO_3 (200 mg) was stirred at room temperature for 12 h. The reaction mixture was then poured on to ice (200 g) and the solid formed was filtered off immediately and washed with an excess of water. The crude product was dried over $CaCl_2$ and recrystallized from ethyl acetate–hexane (1:9) to give colourless crystals of the title compound.

Crystal data

$C_{22}H_{18}Br_2N_2O_2S$
$M_r = 534.26$
Triclinic, $P\overline{1}$
$a = 12.436$ (3) Å
$b = 12.715$ (3) Å
$c = 16.073$ (3) Å
$\alpha = 70.13$ (3)°
$\beta = 69.23$ (3)°
$\gamma = 66.22$ (3)°
$V = 2116.2$ (10) Å^3
$Z = 4$
$D_x = 1.677$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
$\theta = 1.4$–25.0°
$\mu = 3.95$ mm^{-1}
$T = 293$ (2) K
Prism, colourless
0.40 × 0.30 × 0.30 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
Non-profiled $\omega/2\theta$ scans
Absorption correction: ψ scan (North *et al.*, 1968)
$T_{\min} = 0.301$, $T_{\max} = 0.384$
7786 measured reflections
7411 independent reflections
3320 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.053$
$\theta_{\max} = 25.0°$
$h = 0 \rightarrow 14$
$k = -13 \rightarrow 15$
$l = -17 \rightarrow 19$
3 standard reflections
frequency: 300 min
intensity decay: 1%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.056$
$wR(F^2) = 0.135$
$S = 0.95$
7411 reflections
559 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0576P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.63$ e Å^{-3}
$\Delta\rho_{\min} = -0.47$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

N1*A*—C8*A*	1.421 (8)	N1*B*—C1*B*	1.398 (8)
N1*A*—C1*A*	1.432 (9)	N1*B*—C8*B*	1.442 (9)
N2*A*—C10*A*	1.391 (8)	N2*B*—C10*B*	1.379 (9)
N2*A*—C9*A*	1.449 (8)	N2*B*—C9*B*	1.448 (9)
O1*A*—S1*A*—O2*A*	119.9 (3)	O2*B*—S1*B*—O1*B*	119.7 (3)
N1*A*—S1*A*—C17*A*	104.9 (3)	N1*B*—S1*B*—C17*B*	105.6 (3)
O2*A*—S1*A*—N1*A*—C1*A*	−46.0 (6)	O2*B*—S1*B*—N1*B*—C1*B*	−48.2 (6)
C10*A*—N2*A*—C9*A*—C8*A*	176.5 (6)	C10*B*—N2*B*—C9*B*—C8*B*	−83.2 (9)
N1*A*—C8*A*—C9*A*—N2*A*	95.5 (8)	N1*B*—C8*B*—C9*B*—N2*B*	−60.5 (10)
O2*A*—S1*A*—C17*A*—C22*A*	−156.1 (6)	O2*B*—S1*B*—C17*B*—C22*B*	−164.8 (6)

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

Cg(PS) denotes the centroid of the phenyl ring bound to the sulfonyl group and *Cg*(PA) denotes that of the aniline ring.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C2*A*—H2*A*···O2*A*	0.96	2.35	2.956 (11)	120
C9*A*—H9*A*···O1*A*	0.96	2.34	2.894 (10)	116
N2*A*—H2*AN*···Br2*A*	0.90	2.64	3.080 (7)	111
C2*B*—H2*B*···O2*B*	0.96	2.36	2.954 (10)	119
C9*B*—H9*D*···O1*B*	0.96	2.48	2.845 (11)	102
N2*B*—H2*BN*···Br2*B*	0.90	2.57	3.044 (7)	114
N2*B*—H2*BN*···O1*B*	0.90	2.32	2.832 (11)	116
C16*A*—H16*C*···Br2*B*$^{\rm i}$	0.96	2.88	3.772 (14)	155
C20*A*—H20*A*···O2*B*$^{\rm ii}$	0.96	2.57	3.217 (10)	125
C5*A*—H5*A*···*Cg*(PS)	0.96	2.78	3.680 (9)	157
C3*B*—H3*B*···*Cg*(PA$^{\rm ii}$)	0.96	2.89	3.763 (13)	151

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

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All the H atoms were fixed geometrically and allowed to ride on their carrier atoms. Owing to the poor diffraction quality of the crystal, the ratio of observed to unique reflections is low (45%).

Data collection: *CAD*-4 *EXPRESS* (Enraf–Nonius, 1994); cell refinement: *CAD*-4 *EXPRESS*; data reduction: *XCAD*4 (Harms & Wocadlo, 1995); 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, 1995).

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