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Trimethyl[3-methyl-1-(*o*-tolenesulfonyl)indol-2-ylmethyl]ammonium iodide and benzyl[3-bromo-1-(phenylsulfonyl)indol-2-ylmethyl]tolylamine

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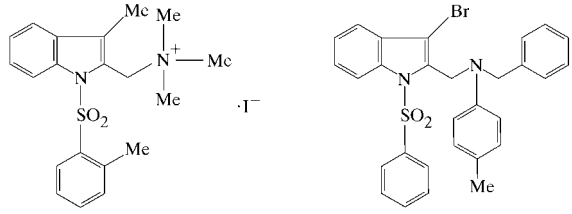
The title compounds, $C_{20}H_{25}N_2O_2S^+\cdot I^-$, (I), and $C_{29}H_{25}BrN_2O_2S$, (II), respectively, both crystallize in space group $P\overline{1}$. The pyrrole ring subtends an angle with the sulfonyl group of 33.6° in (I) and 21.5° in (II). The phenyl ring of the sulfonyl substituent makes a dihedral angle with the best plane of the indole moiety of 81.6° in (I) and 67.2° in (II). The lengthening or shortening of the C—N bond distances in both compounds is due to the electron-withdrawing character of the phenylsulfonyl group. The S atoms are in distorted tetrahedral configurations. The molecular structures are stabilized by C—H···O and C—H···I interactions in (I), and by C—H···O and C—H···N interactions in (II).

Comment

Indoles are known for their important chemical, medicinal and physiological activities, and they are of biological interest as antitumour-active substances. Structural studies of some derivatives of indole have been useful in understanding the molecular mechanisms controlling anxiety, convulsions, memory, learning and sleep in animals. Indoles have been of interest for many years, since a large number of natural products contain these heterocyclic nuclei, and they are found in a number of pharmaceutical products, fragrances and dyes (Padwa *et al.*, 1999). Most of them are found to possess antimicrobial, anti-inflammatory (El-Sayed *et al.*, 1986) and muscle-relaxant properties. A variety of [*b*]annellated indoles are of biological interest as antitumour-active substances (Schollmeyer *et al.*, 1995). Spiro-indole derivatives exhibit antibacterial and antifungal properties (Sehgal *et al.*, 1994). Against this background, and in order to obtain detailed information on molecular conformations in the solid state, X-ray studies of the title compounds, (I) and (II), have been carried out and the results are presented here.



Figs. 1 and 2 show the molecules of (I) and (II) with their atomic numbering schemes. The two compounds are discussed in parallel below, for ease of comparison. Selected geometric parameters are given in Tables 1 and 3 for (I) and (II), respectively.

In both compounds, the indole ring system is not strictly planar. The angular disposition of the bonds about the S atom shows significant deviation from that of a regular tetrahedron, with the largest deviations being seen for the O—S—O [O2—S—O1 119.69 (14)° in (I) and 120.5 (2)° in (II)] and O—S—N angles [O1—S—N1 106.57 (11)° in (I) and 107.4 (2)° in (II)]. The widening of the angles may be due to repulsive interactions between the two short S=O bonds, similar to what is observed in related structures (Rodriguez *et al.*, 1995).

The S—N bond distances [S—N1 1.665 (9) Å in (I) and 1.677 (4) Å in (II)] lie within the expected range of 1.63–1.69 Å (Kálmán *et al.*, 1981). The average S—O, S—C, and S—N distances are 1.435, 1.776 and 1.674 Å, respectively, in (I), and 1.409, 1.746 and 1.676 Å, respectively, in (II); these are

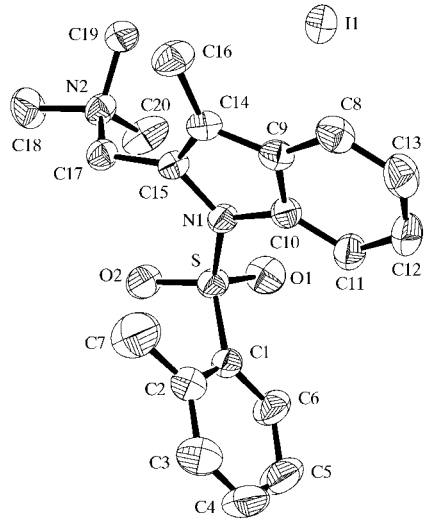


Figure 1
A view of the molecule of (I) with the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms have been omitted for clarity.

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comparable with the values found in *N*-phenylsulfonamides (Gomes *et al.*, 1993). The narrowing of the N1—S—C1 angle to 106.32 (11)° in (I) and of the N1—S—C9 angle to 106.3 (2) in (II) from the ideal tetrahedral value is attributed to the Thorpe–Ingold effect (Bassindale, 1984).

The O1—S—N1—C10 and O1—S—C1—C6 torsion angles in (I) and the O1—S—N1—C1 and O1—S—C9—C10 torsion angles in (II) describe the conformation of the phenylsulfonyl group with respect to the indole system, and the best planes of the indole and phenyl rings form a dihedral angle of 81.6° in (I) and 67.2° in (II), as observed in similar structures (Sankaranarayanan *et al.*, 2000).

The difference in C—N bond lengths may be due to the electron-withdrawing character of the phenylsulfonyl group (Govindasamy *et al.*, 1998). The angular distortion of the benzene ring of the indole moiety is a characteristic property. The substitution of the phenylsulfonyl group at atom N1 results in an enhancement of the C—N bond lengths. The sum of the angles around N1 is 360° for (I) and 359.7° for (II), indicating sp^2 hybridization.

The positions of methyl atom C16 on C14 in (I) and of the Br atom on C2 in (II) do not deviate significantly from the least-squares planes through the pyrrole ring. The average value of the bond lengths in all of the six-membered rings is 1.391 Å, but there are significant deviations among the individual values. In (I), the angles at C8 and C11 are 118.3 (3) and 116.7 (2)°, respectively, and around C13 and C10 they are 121.3 (2) and 122.5 (3)°, respectively. In (II), the angles around C8 and C5 are 120.4 (5) and 121.1 (5)°, respectively, and around C7 and C4 they are 116.8 (5) and 118.0 (5)°, respectively. This may be due to the fusion of the pyrrole ring to the six-membered benzene ring.

The C14—C16 bond length of 1.499 (3) Å in (I) and the C2—Br bond length of 1.873 (4) Å in (II) are comparable with values found in the literature (Allen *et al.*, 1987). The strain is due to angular rather than bond-length distortion. A similar effect has also been observed by Sankaranarayanan *et al.* (2000). The dihedral angle between the pyrrole and benzene rings is 1.79° in (I) and 2.18° in (II).

The orientation of the indole substituent is influenced by a weak C11—H11···O1 interaction in (I), defined by the C11—C10—N1—S torsion angle, and a weak C7—H7···O2 interaction in (II), defined by the C7—C8—N1—S torsion angle, while the orientation of the phenyl ring bound to the sulfonyl group is governed by a C6—H6···O1 interaction in (I), defined by the O1—S—C1—C6 torsion angle, and by a C14—H14···O2 interaction in (II), defined by the O2—S—C9—C14 torsion angle. In addition to van der Waals interactions, the packing of the molecules in the unit cell is governed by C—H···O and C—H···I interactions in (I), and by C—H···O and C—H···N interactions in (II). Details of these interactions are given in Tables 2 and 4 for (I) and (II), respectively.

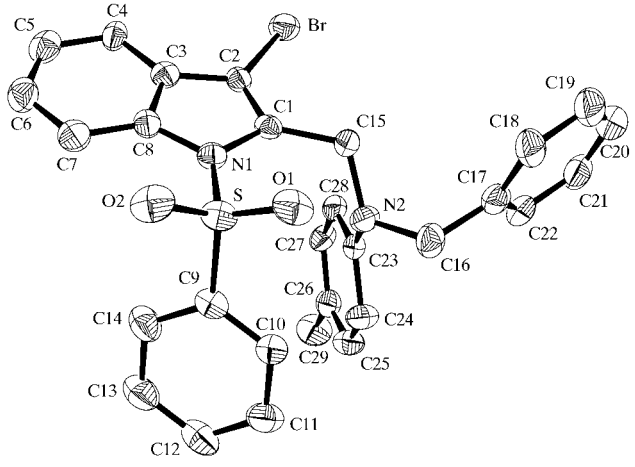

Figure 2
A view of the molecule of (II) with the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms have been omitted for clarity.

Experimental

For the preparation of compound (I), *n*-BuLi (6.25 ml, 1.6*M* in hexane, 5 mmol) and trimethylethylenediamine (0.2 ml) were added to a solution of 1-phenylsulfonyl-3-methyl-2-(*N*,*N*-dimethylamino)-methylindole (1.64 g, 5 mmol) in dry tetrahydrofuran (50 ml) under nitrogen and the mixture stirred at 195 K for 30 min. To the cherry-red reaction mixture, methyl iodide (0.95 ml, 15 mmol) was added. After stirring at 195 K for 2 h, the reaction mixture was heated slowly to room temperature and after 1 h, it was quenched with a saturated solution of NH_4Cl (20 ml). It was then extracted with dichloromethane (3 × 50 ml) and dried ($MgSO_4$). Removal of the solvent followed by column-chromatographic purification [silica gel, ethyl acetate–hexane (1:9)] afforded the pure quaternary salt, (I). For the preparation of compound (II), a solution of 1-phenylsulfonyl-2-bromomethyl-3-bromoindole (4.29 g, 10 mmol) and *N*-benzyl-*p*-toluidine (2 equivalents) in dry dimethylformamide (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 which formed was filtered off and washed with an excess of water. The crude product was dried over $CaCl_2$ and recrystallization from ethyl acetate–hexane (1:9) gave compound (II).

Compound (I)

Crystal data

$C_{20}H_{25}N_2O_2S^+\cdot I^-$
M_r = 484.38
Triclinic, $P\overline{1}$
a = 7.0259 (1) Å
b = 12.2874 (2) Å
c = 13.0484 (3) Å
α = 80.316 (1)°
β = 79.508 (1)°
γ = 74.462 (1)°
V = 1058.64 (3) Å^3
Z = 2
D_x = 1.520 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 4122 reflections
θ = 1.6–28.2°
μ = 1.63 mm^{-1}
T = 293 (2) K
Block, yellow
0.48 × 0.42 × 0.40 mm

Data collection

Siemens SMART CCD area-detector diffractometer
ω scans
Absorption correction: empirical (*SADABS*; Sheldrick, 1996)
T_{min} = 0.472, T_{max} = 0.522
7395 measured reflections
5062 independent reflections
4494 reflections with $I > 2\sigma(I)$
R_{int} = 0.024
θ_{max} = 28.2°
$h = -9 \rightarrow 6$
$k = -16 \rightarrow 16$
$l = -16 \rightarrow 17$
Intensity decay: <2%

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0520P)^2 + 0.0768P]$ where $P = (F_o^2 + 2F_c^2)/3$
$R[F^2 > 2\sigma(F^2)] = 0.032$	$(\Delta/\sigma)_{max} = 0.002$
$wR(F^2) = 0.087$	$\Delta\rho_{max} = 0.84$ e Å^{-3}
$S = 0.99$	$\Delta\rho_{min} = -0.55$ e Å^{-3}
5062 reflections	Extinction correction: *SHELXL*97
226 parameters	Extinction coefficient: 0.0213 (13)
H-atom parameters constrained	

Table 1
Selected geometric parameters (Å, °) for (I).

S—O1	1.429 (2)	N1—C15	1.438 (3)
S—O2	1.4311 (18)	N2—C20	1.496 (3)
S—N1	1.6659 (18)	N2—C19	1.499 (3)
S—C1	1.775 (2)	N2—C18	1.509 (3)
N1—C10	1.416 (2)		
O1—S—O2	119.69 (14)	N1—S—C1	106.32 (11)
O1—S—N1	106.57 (11)	C10—N1—C15	107.92 (15)
O2—S—N1	107.13 (10)	C10—N1—S	120.47 (13)
O1—S—C1	108.44 (13)	C15—N1—S	131.13 (15)
O2—S—C1	107.96 (11)	C20—N2—C19	107.5 (2)
O1—S—N1—C10	−61.93 (18)	O1—S—C1—C6	−17.68 (19)
O2—S—N1—C10	168.84 (16)	O1—S—C1—C2	169.2 (2)
C1—S—N1—C10	53.60 (18)	O2—S—C1—C2	−59.7 (2)
O1—S—N1—C15	127.0 (2)	C15—N1—C10—C11	−179.3 (2)
O2—S—N1—C15	−2.2 (2)	S—N1—C10—C11	7.7 (3)

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C19—H19*A*···I1	0.96	2.98	3.882 (3)	157
C19—H19*B*···I1^{i}	0.96	2.95	3.900 (3)	172
C20—H20*A*···O2	0.96	2.41	3.078 (4)	127
C17—H17*B*···O2	0.97	2.26	2.928 (3)	125
C6—H6···O1	0.93	2.41	2.837 (2)	108
C11—H11···O1	0.93	2.69	3.191 (3)	114

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

Compound (II)

Crystal data

$C_{29}H_{25}BrN_2O_2S$	$Z = 2$
$M_r = 545.48$	$D_x = 1.471$ Mg m^{-3}
Triclinic, $P\overline{1}$	Mo $K\alpha$ radiation
$a = 9.742$ (5) Å	Cell parameters from 25 reflections
$b = 12.211$ (5) Å	$\theta = 1.9$–$25.0°$
$c = 12.446$ (5) Å	$\mu = 1.78$ mm^{-1}
$\alpha = 61.362$ (5)°	$T = 293$ (2) K
$\beta = 99.119$ (5)°	Block, yellow
$\gamma = 108.610$ (5)°	0.48 × 0.34 × 0.28 mm
$V = 1231.5$ (10) Å^3	

Data collection

Enraf–Nonius CAD-4 diffractometer	$R_{int} = 0.020$
ω scans	$\theta_{max} = 25°$
Absorption correction: ψ scan (North *et al.*, 1968)	$h = 0 \rightarrow 11$
$T_{min} = 0.481$, $T_{max} = 0.635$	$k = -14 \rightarrow 13$
4619 measured reflections	$l = -14 \rightarrow 14$
4340 independent reflections	3 standard reflections
2645 reflections with $I > 2\sigma(I)$	frequency: 120 min
	intensity decay: <2%

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0520P)^2 + 0.0768P]$ where $P = (F_o^2 + 2F_c^2)/3$
$R[F^2 > 2\sigma(F^2)] = 0.045$	$(\Delta/\sigma)_{max} = 0.007$
$wR(F^2) = 0.146$	$\Delta\rho_{max} = 0.40$ e Å^{-3}
$S = 0.89$	$\Delta\rho_{min} = -0.44$ e Å^{-3}
4340 reflections	
317 parameters	
H-atom parameters constrained	

Table 3
Selected geometric parameters (Å, °) for (II).

Br—C2	1.873 (4)	S—C9	1.747 (4)
S—O1	1.416 (4)	N1—C8	1.410 (6)
S—O2	1.421 (4)	N1—C1	1.419 (5)
S—N1	1.677 (4)	N2—C15	1.466 (5)
O1—S—O2	120.5 (2)	O2—S—C9	107.4 (2)
O1—S—N1	107.4 (2)	N1—S—C9	106.30 (19)
O2—S—N1	105.3 (2)	C8—N1—S	124.7 (3)
O1—S—C9	109.0 (2)	C1—N1—S	126.9 (3)
O1—S—N1—C8	−149.1 (3)	S—N1—C8—C7	−9.2 (6)
O2—S—N1—C8	−19.5 (4)	O1—S—C9—C10	−0.8 (5)
O1—S—N1—C1	23.8 (4)	O2—S—C9—C10	−132.9 (4)
O2—S—N1—C1	153.4 (3)	O2—S—C9—C14	44.0 (5)

Table 4
Hydrogen-bonding ahd short-contact geometry (Å, °) for (II).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C10—H10···N2	0.93	2.87	3.268 (7)	107
C14—H14···O2	0.93	2.81	3.025 (6)	95
C7—H7···O2	0.93	2.35	2.876 (7)	116

For both compounds, all H atoms were fixed geometrically and allowed to ride on their parent atoms, with C—H distances in the range 0.93–0.97 Å, and with $U_{iso}(H) = 1.5U_{eq}(C)$ for methyl H atoms and $1.2U_{eq}(C)$ for other H atoms.

For compound (I), data collection: *SMART* (Siemens, 1996); cell refinement: *SAINT* (Siemens, 1996); data reduction: *SAINT*. For compound (II), data collection: *CAD*-4 *EXPRESS* (Enraf–Nonius, 1994); cell refinement: *CAD*-4 *EXPRESS*; data reduction: *XCAD*4 (Harms & Wocadlo, 1995). For both compounds, program(s) used to solve structure: *SIR*92 (Altomare *et al.*, 1993); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*-3 (Farrugia, 1997); software used to prepare material for publication: *SHELXL*97 and *PARST* (Nardelli, 1995).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1573). Services for accessing these data are described at the back of the journal.

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