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2-Bromo-*N*-(*p*-toluenesulfonyl)pyrrole

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Key indicators

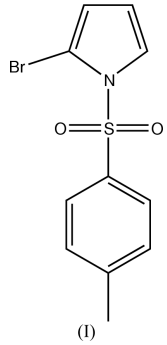
Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.006 Å
Disorder in main residue
R factor = 0.046
wR factor = 0.089
Data-to-parameter ratio = 16.8

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

The title compound, $C_{11}H_{10}BrNO_2S$, crystallizes in a columnar structure consisting of interdigitated C—H···O doubly bonded chains. The columns pack in a herring-bone fashion and are linked through additional weak hydrogen bonding. The structure is very nearly isomorphous to one in which the bromo substituent on the pyrrole ring is replaced by a chloromethyl group, in spite of the difference in size, shape and interactions involving these two groups.

Comment

Since the discovery of cannabimimetic properties in selected aminoalkylindoles by the Sterling–Winthrop group (Bell *et al.*, 1991), researchers around the world have taken on the challenge of finding a pharmacophore for the cannabinoid receptor that encompasses the four main classes of cannabinoid ligands, *viz*. aminoalkylindoles, endogenous cannabinoids, non-traditional cannabinoids and traditional cannabinoids (Huffman & Lainton, 1996). It has been proposed that aromatic stacking may play an important role in the affinity of highly aromatic ligands, such as the aminoalkylindoles (Reggio *et al.*, 1998). In an attempt to test the significance of the benzenoid moiety of the indole, a series of *N*-alkyl-3-(1-naphthoyl)pyrroles was synthesized and shown to possess reduced affinity for the cannabinoid receptor compared with similarly substituted indoles (Lainton *et al.*, 1995). To follow up on this development, a series of *N*-alkyl-2-phenyl-3-(1-naphthoyl)pyrroles was synthesized and found to exhibit significantly increased affinity over the previous pyrrole series (Huffman & Isherwood, 2003). In order to further study the effects promoted by the 2-aryl functionality, an easily derivatizable synthon of 2-arylpyrrole is required. One such route proceeds through *N*-(*p*-toluenesulfonyl)-2-bromopyrrole, (I), the subject of this paper.



(I)

The bonding parameters of (I) (Fig. 1) are very similar to those of related tosylpyrroles (Abell *et al.*, 1998), pyrrolidines (Sambyal *et al.*, 1995; Gupta *et al.*, 1995), and other related

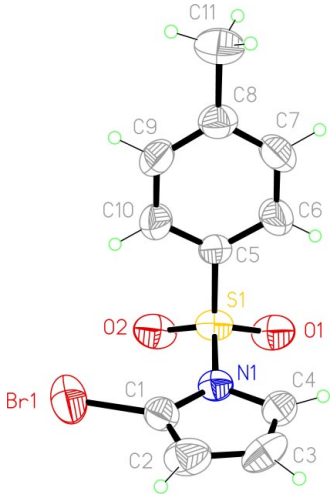


Figure 1
The molecular structure of (I). Displacement ellipsoids are drawn at the 50% probability level and H atoms are of arbitrary radii. Only one set of the disordered methyl H atoms is shown.

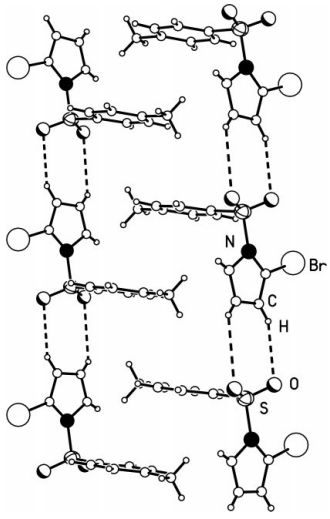


Figure 2
C—H···O hydrogen-bonded chains of (I), interdigitated to form columns.

sulfonylamides (Ohwada *et al.*, 1998). As opposed to the majority of the latter, the bonding about the N atom is nearly planar with a bond angle sum of 358.4°, while the average value for 349 sulfonylamides was found to be 352.4° (Ohwada *et al.*, 1998). The pyrrole ring in (I) has a slight envelope conformation, the N atom lying 0.041 (6) Å out of the plane of the four ring C atoms which are planar within 0.0005 Å. The molecular conformation can be described by the dihedral angles between three-atom planes consisting of the pyrrole bridgehead (C1/N1/C4), the sulfur linkage between the two rings (N1/S1/C5), and the aryl bridgehead (C6/C5/C10). Sulfonylamides often have a pseudo-staggered conformation with the sulfonyl O atoms equally disposed to one side of a given ring plane and the S-bridgehead vector of the other ring to the opposite side. In this conformation, both ring planes are orthogonal to the sulfur linkage plane (Abell *et al.*, 1998). This

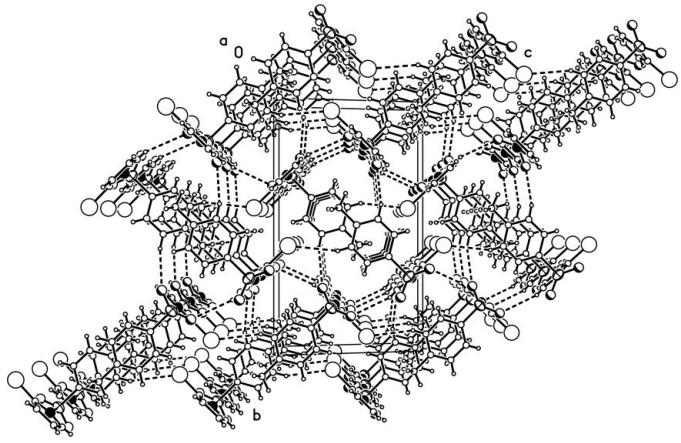


Figure 3
Herring-bone packing of columns of (I), viewed down the *a* axis.

is indeed the case for the pyrrole plane, but the aryl ring is rotated to a value of 83.5 (4)°. The sulfonyl group is in a pseudo-staggered orientation with respect to the aryl group, with a dihderal angle of 89.3 (4)° between the three-atom planes C6/C5/C10 and C5/S1/N1, but deviates with respect to the pyrrole ring as the dihedral angle between the C5/S1/N1 and C1/N1/C4 planes is 83.5 (4)°. This deviation is most likely due to steric interaction between the Br atom on the pyrrole ring and a neighboring sulfonyl O atom.

The crystal packing is dominated by double C—H···O hydrogen bonds between the C—H bonds at the 3- and 4-positions of the pyrrole ring with the sulfonyl O atoms of a molecule related by translation along the *a* axis. The resulting ribbons mesh with those related by inversion symmetry ($\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$) to form a column with interdigitated aryl groups (Fig. 2). The columns pack in a herring-bone fashion, with C—H···Br and additional C—H···O interactions linking columns related by symmetry (Fig. 3). Although not discussed, the packing of *N*-tosyl-2-chloromethylpyrrole (Abell *et al.*, 1998) is almost identical to that observed for (I), and, in fact, the two structures are nearly isomorphous.

Experimental

The title compound, (I), was synthesized in a one-pot procedure that first brominates the pyrrole, and then protects it before the compound is removed from solution. A detailed experimental procedure for this synthesis will be published elsewhere. The compound was then purified through recrystallization from 2-propanol, and X-ray quality crsytals were grown from methylene chloride.

Crystal data

$C_{11}H_{10}BrNO_2S$
M_r = 300.17
Monoclinic, $P2_1/n$
a = 7.6482 (13) Å
b = 16.307 (2) Å
c = 10.2114 (17) Å
β = 110.233 (3)°
V = 1195.0 (3) Å^3
Z = 4
D_x = 1.668 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 7533 reflections
θ = 2.8–26.4°
μ = 3.60 mm^{-1}
T = 293 (2) K
Plate, colorless
0.35 × 0.20 × 0.10 mm

Data collection

MSC/Rigaku Mercury AFC-8*S* CCD diffractometer	2437 independent reflections
ω scans	2006 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (*REQAB*; Jacobson, 1998)	$R_{int} = 0.029$
$T_{min} = 0.454$, $T_{max} = 0.698$	$\theta_{max} = 26.4^\circ$
11 515 measured reflections	$h = -9 \rightarrow 9$
	$k = -20 \rightarrow 19$
	$l = -11 \rightarrow 12$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.001P)^2 + 3.06P]$ where $P = (F_o^2 + 2F_c^2)/3$
$R[F^2 > 2\sigma(F^2)] = 0.046$	$(\Delta/\sigma)_{max} = 0.001$
$wR(F^2) = 0.089$	$\Delta\rho_{max} = 0.48$ e Å^{-3}
$S = 1.00$	$\Delta\rho_{min} = -0.75$ e Å^{-3}
2437 reflections	
145 parameters	
H-atom parameters constrained	

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

D—H···A	D—H	H···A	D···A	D—H···A
C2—H2*A*···O2^{i}	0.93	2.58	3.383 (5)	145
C3—H3*A*···O1^{i}	0.93	2.81	3.585 (5)	141
C4—H4*A*···O2^{ii}	0.93	2.55	3.447 (5)	161
C7—H7*A*···Br1^{iii}	0.93	3.11	3.977 (4)	155
C9—H9*A*···O1^{iv}	0.93	2.80	3.622 (5)	148

Symmetry codes: (i) $x-1, y, z$; (ii) $x-\frac{1}{2}, \frac{3}{2}-y, z-\frac{1}{2}$; (iii) $x, y, z-1$; (iv) $\frac{3}{2}-x, y-\frac{1}{2}, \frac{3}{2}-z$.

All H atoms were refined with isotropic displacement parameters, except for those of the methyl group, which were found to be disordered over two rotationally related sites. Two sets of half-occupancy H atoms were constrained to ride on the methyl C atom at positions optimized from those obtained from a difference Fourier map.

Data collection: *CrystalClear* (Molecular Structure Corporation/Rigaku, 2001); cell refinement: *CrystalClear*; data reduction: *CrystalClear*; program(s) used to solve structure: *SHELXTL-Plus* (Sheldrick, 2000); program(s) used to refine structure: *SHELXTL-Plus*; molecular graphics: *SHELXTL-Plus*; software used to prepare material for publication: *SHELXTL-Plus*.

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