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N-(*p*-Nitrophenylsulfonyl)-1*H*-pyrrole

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Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.003 Å
R factor = 0.053
wR factor = 0.153
Data-to-parameter ratio = 18.6

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

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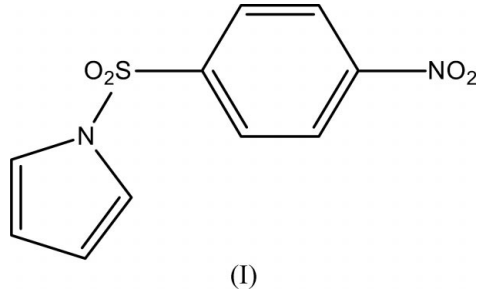
In the title compound, $C_{10}H_8N_2O_4S$, the dihedral angle between the pyrrole and benzene rings is 77.9 (1)°. Intermolecular C—H···O hydrogen bonds stabilize the crystal structure, forming molecular chains extending approximately parallel to the *c* axis and stacked along the *b* axis.

Comment

The [4 + 2]-cycloaddition reaction between pyrroles and dienophiles has been shown to be a general method for the synthesis of 7-azabicyclo[2.2.1]hepta-2,5-diene and 7-azabicyclo[2.2.1]hepta-2-ene derivatives (Trudell & Chen, 1996; Corey & Loh, 1993; Jung & Rohloff, 1984). However, pyrrole is a very poor diene for the [4+2]-cycloaddition reaction and usually reacts with alkenyl and acetylenic dicarboxylic acid derivatives to give Michael addition products.

When an electron-withdrawing group [such as CO_2Me, COMe, $SO_2C_6H_4Me$(Ts) or $CONH_2$] is attached to the pyrrole N atom, the aromatic ring is found to be more reactive as a diene toward acetylenic dienophiles (Drew *et al.*, 1985; Shen & Huang, 1993; Napalitano *et al.*, 1997). However, Michael addition products are still found to be the major products of these reactions.



(I)

The pyrrole derivative of a diene, *viz.* *N*-butoxycarbonylpyrrole, has been converted into 7-(*tert*-butoxycarbonyl)-7-azabicyclo[2.2.1]heptan-2-one *via* cycloaddition with methyl 3-bromopropiolate. This was then used for the synthesis of racemic epibatidine (Zhang & Trudell, 1996). The title compound, (I), may be a useful diene in cycloadditions and may also be a useful starting material for the preparation of biologically important compounds such as epibatidine.

The molecular structure of the title compound, (I), is shown in Fig. 1. The steric interaction between H1 attached to C1 and atom O3 [O3···H1 = 2.56 (3) Å] results in an enlarged S1—N1—C1 angle [125.9 (2)°]. It is well known that nitro substituents are very strong electron-withdrawing groups, so the endocyclic C7—C8—C9 angle [123.1 (2)°] is also enlarged. The back donation of the lone pair of electrons of atom N1, and also the electron-withdrawing character of the nitro-

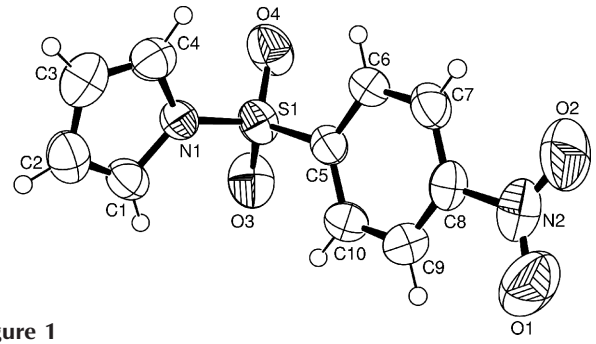


Figure 1
An *ORTEP*-3 (Farrugia, 1997) drawing of the title molecule, with the atom-numbering scheme. The displacement ellipsoids are drawn at the 50% probability level.

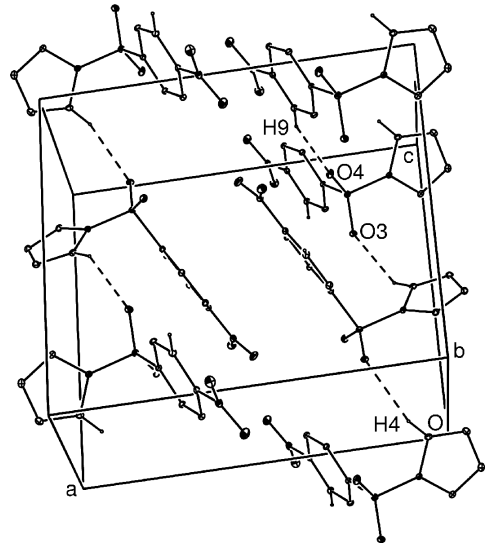


Figure 2
A packing diagram of (I). Dashed lines indicate hydrogen bonds. H atoms not involved in hydrogen bonds have been omitted.

phenylsulfonyl group, affect the bond lengths N1—S1 [1.654 (2) Å] and S1—C5 [1.762 (2) Å]. On the other hand, the electron-withdrawing character of the nitro group has an influence on the C8—N2 bond length [1.476 (3) Å].

The pyrrole and benzene rings are each planar and the dihedral angle between their least-squares planes is 77.9 (1)°. In the pyrrole ring, there is a pseudo-twofold axis passing through atom C2 and the mid-point of the N1—C4 bond, as is evident from the torsion angles (Table 1). The geometrical features of (I) are similar to those of 1-phenylsulfonylpyrrole (Beddoes *et al.*, 1986), 3-benzoyl-1-tosylpyrrole (Erickson *et al.*, 1992), *N*-(1-benzenesulfonyl-4-acetylpyrrol-3-yl)acetamide (Grossie *et al.*, 2001) and 2-bromo-*N*-(*p*-toluenesulfonyl)pyrrole (Knight *et al.*, 2003).

Intermolecular C—H···O hydrogen bonds (Table 2) stabilize the crystal structure, forming molecular chains extending approximately parallel to the *c* axis and stacked along the *b* axis (Fig. 2).

Experimental

The title compound was prepared according to a literature method (Wasley & Chan, 1973). *p*-Nitrobenzenesulfonamide (5.0 g, 25.0 mmol), 2,5-dimethoxytetrahydrofuran (4 ml, 30 mmol) and glacial acetic acid (27 ml) were combined and heated under reflux for 12 h. The reaction mixture was cooled to 293 K, poured into ice-water (50 ml) and stirred for 30 min. The solidified product was collected by filtration and recrystallized from ethanol (yield 4.4 g, 71%; m.p. 415 K).

Crystal data

$C_{10}H_8N_2O_4S$
$M_r = 252.24$
Monoclinic, $P2_1/c$
$a = 12.7169$ (17) Å
$b = 7.5317$ (13) Å
$c = 11.2959$ (12) Å
$\beta = 93.381$ (12)°
$V = 1080.0$ (3) Å^3
$Z = 4$
$D_x = 1.551$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
$\theta = 15$–22°
$\mu = 0.30$ mm^{-1}
$T = 293$ (2) K
Block, light yellow
0.30 × 0.25 × 0.15 mm

Data collection

Siemens *P*4 diffractometer
Non-profiled ω scans
Absorption correction: none
3587 measured reflections
3452 independent reflections
2611 reflections with $I > 2\sigma(I)$
$R_{int} = 0.020$
$\theta_{max} = 31.0°$
$h = 0 \rightarrow 18$
$k = 0 \rightarrow 10$
$l = -16 \rightarrow 16$
3 standard reflections
every 50 reflections
intensity decay: 1%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.053$
$wR(F^2) = 0.153$
$S = 1.08$
3452 reflections
186 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.0643P)^2 + 0.3051P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.23$ e Å^{-3}
$\Delta\rho_{min} = -0.32$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

S1—N1	1.6537 (18)	N2—O1	1.218 (3)
S1—O3	1.4277 (18)	N2—O2	1.218 (3)
S1—O4	1.4215 (19)	N2—C8	1.476 (3)
S1—C5	1.762 (2)	C1—C2	1.342 (4)
N1—C1	1.394 (3)	C2—C3	1.415 (4)
N1—C4	1.393 (3)	C3—C4	1.335 (4)
O3—S1—N1	105.90 (10)	C4—N1—S1	125.58 (16)
O3—S1—C5	108.63 (11)	O1—N2—O2	124.3 (3)
O4—S1—O3	121.64 (13)	O1—N2—C8	118.6 (3)
O4—S1—N1	106.26 (11)	O2—N2—C8	117.1 (2)
O4—S1—C5	108.47 (10)	C2—C1—N1	107.2 (2)
N1—S1—C5	104.66 (9)	C1—C2—C3	108.4 (2)
C1—N1—S1	125.90 (16)	C4—C3—C2	108.4 (2)
C4—N1—C1	108.4 (2)	C3—C4—N1	107.6 (2)
C4—N1—C1—C2	1.0 (2)	N1—C4—C3—C2	1.0 (3)
C1—N1—C4—C3	−1.3 (2)	C1—C2—C3—C4	−0.4 (3)
N1—C1—C2—C3	−0.4 (3)		

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

D—H···A	D—H	H···A	D···A	D—H···A
C4—H4···O3^{i}	0.93 (3)	2.56 (2)	3.359 (3)	145 (2)
C9—H9···O4^{ii}	0.92 (3)	2.41 (3)	3.247 (3)	152 (2)

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

The H atoms were located in a difference synthesis and refined isotropically [C—H = 0.85 (3)–0.94 (3) Å].

Data collection: *XSCANS* (Siemens, 1996); cell refinement: *XSCANS*; data reduction: *SHELXTL* (Bruker, 1997); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*-3 (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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