

2-[[[(4-Methylphenyl)sulfonyl]amino]-  
phenyl 4-methylbenzenesulfonateG. L. Morgans, S. M. Scalzullo, M. A. Fernandes,\* J. P.  
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The title compound,  $C_{20}H_{19}NO_5S_2$ , crystallizes as an almost 2:1 mixture of two molecular orientations (described as Orient-A and Orient-B). The consequences of these two orientations is the formation of three types of N—H...O hydrogen-bonded dimers in which the (Orient-A + Orient-A) dimers are likely to be the most stable, while the mixed (Orient-A + Orient-B) dimers are more frequent. Extra interactions in the form of C—H...O and C—H... $\pi$  interactions act to further stabilize these dimers and probably allow the less energetically favourable (Orient-A + Orient-B) and (Orient-B + Orient-B) hydrogen-bonded dimers to exist by preventing their conversion to (Orient-A + Orient-A)-only hydrogen-bonded dimers during the crystal-growth process.

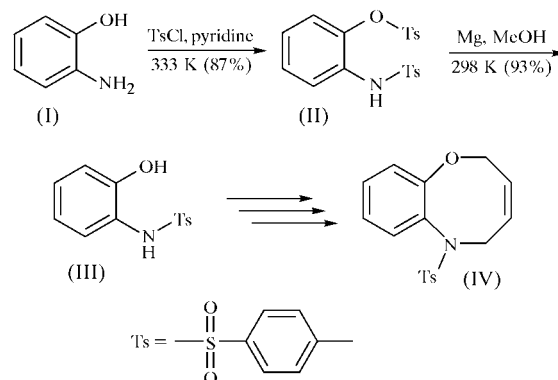
## Comment

Benzannulated heterocycles are interesting compounds that play important structural roles in natural products and man-made pharmaceuticals. Our research group has used ring-closing metathesis (RCM) and isomerization-RCM strategies to synthesize benzannulated heterocycles (van Otterlo, Morgans *et al.*, 2004, 2005; van Otterlo, Ngidi *et al.*, 2004, 2005).

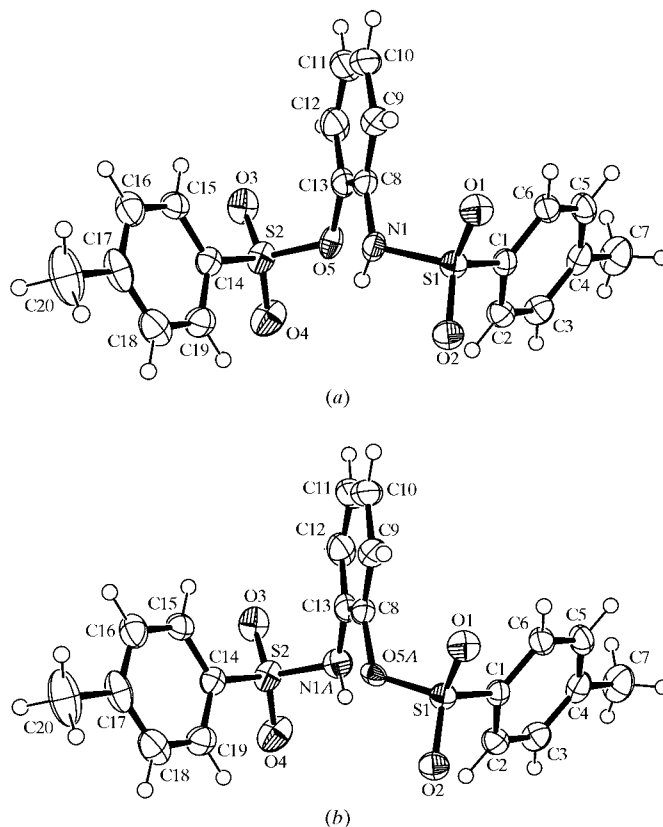
During the synthesis of heterocycles, such as (IV) (see scheme), containing both N and O atoms in the benzofused portion, 2-aminophenol, (I), has to be protected initially as its ditosyl derivative, (II). Selective cleavage of the S—O bond, with magnesium in methanol (Sridhar *et al.*, 1998), then affords compound (III), which can be converted to the protected 6-[[[(4-methylphenyl)sulfonyl]-5,6-dihydro-2H-1,6-benzoxazocine, (IV), *via* a number of steps (van Otterlo, Morgans *et al.*, 2004; Ibrahim *et al.*, 2002). As compound (II) is crystalline, it was decided that it would be interesting to investigate its structure in the solid state.

Compound (II) crystallizes as a disordered arrangement in which atoms N1 and O5 are interchanged in two orientations such that the molecule shown in Fig. 1(a) (Orient-A) is superimposed on the molecule shown in Fig. 1(b) (Orient-B). The ratio of Orient-A to Orient-B is about 0.63 (2):0.37 (2).

Visually the molecule has a pseudo-twofold axis passing through the aromatic ring defined by atoms C8–C13, and one would therefore expect the molecule to crystallize on a twofold axis (a special position in space groups containing this

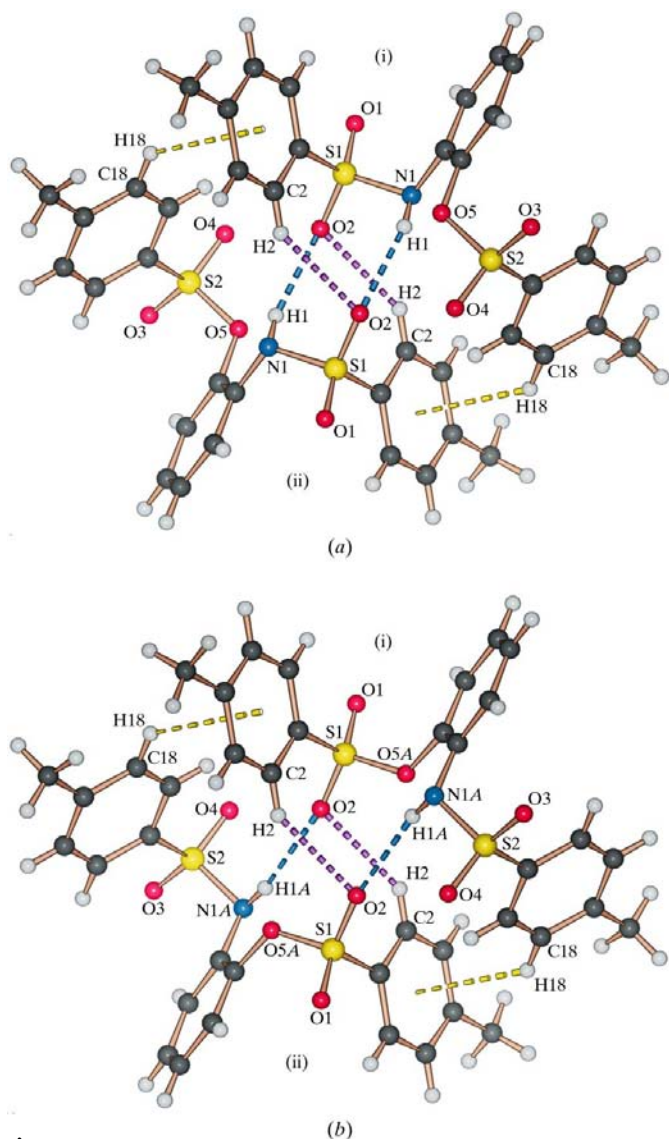


symmetry), leading to the observed orientational disorder. However, the compound crystallizes instead in the space group  $P\bar{1}$  with one molecule in the asymmetric unit. Comparison of some geometric parameters between the sulfonyl groups and the attached benzene rings (C1–C6 *versus* C14–C19) indicates that the torsion angles on the two sides differ by more than  $10^\circ$  (Table 1) and hence indicate the absence of a molecular twofold axis.



**Figure 1**  
Views of the two orientations of the molecule of (II), *viz.* (a) Orient-A and (b) Orient-B, showing the atom-numbering schemes. These are superimposed on each other in the crystal structure. Displacement ellipsoids are drawn at the 50% probability level. H atoms are shown with an arbitrary radius.

The crystal structure of (II) is stabilized by both intra- and intermolecular classical and weak hydrogen bonding (Table 2; for simplicity the very extensive intramolecular hydrogen bonding has been omitted from this table but can be found in the CIF). The dominant intermolecular interaction in the structure is an N—H···O hydrogen bond between a pair of molecules forming a hydrogen-bonded dimer. The morphology of this hydrogen-bonded network differs significantly between the two molecular orientations, though the overall appearance is very similar (Fig. 2). For Orient-A, the N—H···O hydrogen bonding (between N1 and O2<sup>ii</sup>; symmetry code as in Table 2) results in a hydrogen-bonded



**Figure 2**  
Hydrogen-bonded dimers in the structure of (II). These diagrams represent the extremes in which (a) Orient-A molecules hydrogen bond to other Orient-A molecules and (b) Orient-B molecules hydrogen bond to other Orient-B molecules. The most frequent real situation is probably a combination of the two. Indicated on the diagrams are the N—H···O (N1A—H1A···O2), C—H···O (C2—H2···O2) and C—H··· $\pi$  interactions for both types of hydrogen-bonded dimer. Molecules (i) and (ii) are at the symmetry positions  $(x, y, z)$  and  $(-x + 2, -y, -z + 1)$ , respectively.

dimer that can be described by the  $R_2^2(8)$  graph set (Fig. 2a). For the alternative orientation (Orient-B), the N—H···O hydrogen bonding (between N1A and O2<sup>ii</sup> in this case) results in a hydrogen-bonded dimer that can be described by the  $R_2^2(14)$  graph set (Fig. 2b). Interestingly, the hydrogen-bond dimer formed by a pair of Orient-A molecules has a  $D\cdots A$  distance of 3.038 (16) *versus* 3.31 (3) Å in the dimer formed by a pair of Orient-B molecules. The shorter  $D\cdots A$  distance between Orient-A molecules implies that this orientation is more stable and this assumption is corroborated by the higher frequency of Orient-A (63% occurrence). Nevertheless, the frequency of the Orient-B orientation is still very high. Rather than the extremes of Orient-A- and Orient-B-only dimers, it is likely that the 'real' average situation in a crystal is a hydrogen-bonded relationship in which Orient-A is about 26% (frequency of Orient-A minus frequency of Orient-B) of the time hydrogen bonded to other Orient-A molecules and the rest of the time hydrogen bonded to Orient-B molecules (37% of the time minus the frequency of Orient-B). This (Orient-A + Orient-B) arrangement would probably not be as energetically unfavourable as Orient-B-only hydrogen-bonded dimers, being made up of one hydrogen bond of each type of orientation, *i.e.* one 3.0 Å and one 3.3 Å intermolecular N—H···O bond. These hydrogen-bonded dimers are further stabilized by C—H··· $\pi$  [C18—H18···Cg(C1—C6)<sup>ii</sup>] and C—H···O (C2—H2···O2) interactions (Fig. 2). The stabilization due to these extra weak interactions is probably also a significant contributor to the stability of the Orient-B dimers as it would probably make the conversion of (Orient-B + Orient-B) (if they exist) and (Orient-B + Orient-A) dimers to Orient-A-only dimers quite difficult.

Finally, all the hydrogen-bonded dimers interact further with neighbouring dimers through C—H···O interactions (C16—H16···O1 and C20—H20C···O1) to form layers perpendicular to the (100) direction.

## Experimental

*p*-Toluenesulfonyl chloride (11.80 g, 62 mmol) was added to 2-amino-phenol (2.25 g, 21 mmol) dissolved in pyridine (50 ml) and stirred under N<sub>2</sub> for 60 h. The pyridine was evaporated and CH<sub>2</sub>Cl<sub>2</sub> (100 ml) was added to the resulting residue. The organic phase was then washed with HCl (0.5 M, 2 × 50 ml), water (50 ml) and brine (50 ml), after which it was dried (MgSO<sub>4</sub>) and evaporated under reduced pressure to afford compound (II) as a yellow solid. This solid was recrystallized from hot EtOH to give white crystals of (II) (6.43 g, 87%, m.p. 410–412 K). NMR:  $\delta_{\text{H}}$  (300 MHz, CDCl<sub>3</sub>) 7.69 (*d*, 2H,  $J = 8.3$  Hz, 2 × Ar—H), 7.64 (*d*, 2H,  $J = 8.3$  Hz, 2 × Ar—H), 7.55 (*dd*, 1H,  $J = 8.1$  and 1.3 Hz, Ar—H), 7.35 (*d*, 2H,  $J = 8.3$  Hz, 2 × Ar—H), 7.19 (*d*, 2H,  $J = 8.3$  Hz, 2 × Ar—H), 7.20–7.15 (*m* partially under *d*, 1H, Ar—H), 7.08 (*br s*, 1H, NH), 6.98 (*dt*, 1H,  $J = 1.3$  and 8.0 Hz, Ar—H), 6.81 (*dd*, 1H,  $J = 8.3$  and 1.3 Hz, Ar—H), 2.48 (*s*, 3H, Ar—CH<sub>3</sub>), 2.36 (*s*, 3H, Ar—CH<sub>3</sub>);  $\delta_{\text{C}}$  (75 MHz, CDCl<sub>3</sub>) 146.4 (Ar—O), 144.0 (Ar—N), 140.2 (Ar—S), 136.2 (Ar—S), 131.4 (Ar—C), 130.1 (Ar—CH), 130.0 (Ar—C), 129.6 (Ar—CH), 128.4 (Ar—CH), 127.9 (Ar—CH), 127.3 (Ar—CH), 125.5 (Ar—CH), 123.3 (Ar—CH), 123.0 (Ar—CH), 21.8 (Ar—CH<sub>3</sub>), 21.5 (Ar—CH<sub>3</sub>);  $\nu_{\text{max}}$  (thin film, NaCl plate, cm<sup>-1</sup>): 3361, 3020, 1599, 1495, 1340, 1293, 1215.

## Crystal data

$C_{20}H_{19}NO_5S_2$	$\gamma = 71.442 (1)^\circ$
$M_r = 417.48$	$V = 969.68 (3) \text{ \AA}^3$
Triclinic, $P\bar{1}$	$Z = 2$
$a = 9.7596 (2) \text{ \AA}$	Mo $K\alpha$ radiation
$b = 10.1025 (2) \text{ \AA}$	$\mu = 0.31 \text{ mm}^{-1}$
$c = 10.7227 (2) \text{ \AA}$	$T = 173 (2) \text{ K}$
$\alpha = 80.173 (1)^\circ$	$0.38 \times 0.24 \times 0.21 \text{ mm}$
$\beta = 76.633 (1)^\circ$	

## Data collection

Bruker SMART CCD area-detector diffractometer	4684 independent reflections
18642 measured reflections	4042 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.027$

## Refinement

$R[F^2 > 2\sigma(F^2)] = 0.038$	92 restraints
$wR(F^2) = 0.105$	H-atom parameters constrained
$S = 1.09$	$\Delta\rho_{\text{max}} = 0.30 \text{ e \AA}^{-3}$
4684 reflections	$\Delta\rho_{\text{min}} = -0.43 \text{ e \AA}^{-3}$
269 parameters	

Table 1

Selected torsion angles ( $^\circ$ ).

C6—C1—S1—O1	-11.43 (16)	C19—C14—S2—O4	22.65 (17)
C2—C1—S1—O2	36.74 (16)	C15—C14—S2—O3	-23.53 (17)

Table 2

Hydrogen-bond and short-contact geometry ( $\text{\AA}$ ,  $^\circ$ ).

Cg1 is the centroid of the C1—C6 ring.

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N1—H1 $\cdots$ O2 <sup>ii</sup>	0.92	2.20	3.038 (16)	151
N1A—H1A $\cdots$ O2 <sup>ii</sup>	0.92	2.43	3.31 (3)	162
C2—H2 $\cdots$ O2 <sup>ii</sup>	0.95	2.50	3.328 (2)	145
C16—H16 $\cdots$ O1 <sup>iii</sup>	0.95	2.65	3.391 (2)	135
C20—H20C $\cdots$ O1 <sup>iv</sup>	0.98	2.63	3.499 (3)	148
C18—H18 $\cdots$ Cg1 <sup>ii</sup>	0.95	2.93	3.642 (2)	133

Symmetry codes: (ii)  $-x + 2, -y, -z + 1$ ; (iii)  $-x + 2, -y + 1, -z + 1$ ; (iv)  $x, y, z + 1$ .

The molecule was found to exhibit orientational disorder with the N1 and O5 positions being disordered. Each of these atoms was refined over two positions, as N1/N1A and O5/O5A, using SADI restraints, while constraining the sum of the final occupancies to unity. The final occupancies were 0.63 (2) for N1 and O5, and 0.37 (2) for N1A and O5A. NH hydrogens (H1 and H1A) were first located in

a Fourier difference map and then positioned geometrically (N—H = 0.92  $\text{\AA}$ ) and treated as riding, with isotropic displacement parameters equal to 1.2 times  $U_{\text{eq}}$  of the parent atoms. H atoms were positioned geometrically and allowed to ride on their respective parent atoms, with C—H bond lengths of 0.95 (aromatic CH) or 0.98  $\text{\AA}$  (CH<sub>3</sub>), and isotropic displacement parameters equal to 1.2 (CH) or 1.5 (CH<sub>3</sub>) times  $U_{\text{eq}}$  of the parent atom.

Data collection: SMART-NT (Bruker, 1998); cell refinement: SAINT-Plus (Bruker, 1999); data reduction: SAINT-Plus; program(s) used to solve structure: SHELXTL (Bruker, 1999); program(s) used to refine structure: SHELXTL; molecular graphics: ORTEP-3 (Farrugia, 1997) and SCHAKAL99 (Keller, 1999); software used to prepare material for publication: PLATON (Spek, 2003) and SHELXTL.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: HJ3033). Services for accessing these data are described at the back of the journal.

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