# 4-Acetamidobenzenesulfonyl azide

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The title compound, $C_8H_8N_4O_3S$, is planar chiral in the solid state. It crystallizes with three independent molecules in the asymmetric unit, two of which have the same chirality and the third is the opposite enantiomer. Partial inversion twinning is present in the crystal which was examined. All three molecules are connected *via* hydrogen bonds between the amide groups, forming a helix around the *b* axis of the unit cell.

## Comment

4-Acetamidobenzenesulfonyl azide (*p*-ABSA), (I), formed by the reaction of the corresponding sulfonyl chloride with sodium azide (Baum *et al.*, 1987), is a commercially available reagent widely used for the base-assisted transfer of the diazo group to active methylene compounds, such as $\beta$-keto esters (Davies *et al.*, 1987; Baum *et al.*, 1987; Taber *et al.*, 2005).



(I)
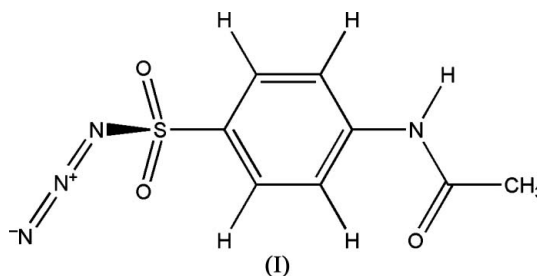
Compound (I) crystallizes in the chiral monoclinic space group $P2_1$ with three crystallographically independent molecules in the asymmetric unit. With two prochiral groups (the amide and the $SO_2N_3$ groups) bonded to a planar core, the *p*-ABSA molecules are planar chiral. In solution, the *pR* and *pS* enantiomers can interconvert rapidly by rotation of either of the substituents. In the solid state, however, this equilibration is frozen. Of the three independent molecules, *A* and *C* have the same sense of chirality; molecule *B*, on the other hand, is in the opposite enantiomeric form, as expressed by the orientation of the amide groups with respect to the position of the azide units (Fig. 1). Not only the general orientation of the substituents between the two enantiomeric forms, but also the overall geometrical features of all three molecules are distinctly different from each other, as expressed mainly by the torsion angles of both the amide as well as the $SO_2N_3$ groups with respect to the aromatic six-membered rings.

The orientation of the S—$N_3$ units for molecules *A*, *B* and *C*, calculated as the dihedral angle between the aromatic ring and the plane formed by atoms C1, S1 and N2, are 83.60 (8), 69.25 (8), and 59.68 (8)°, respectively. Thus, for molecules *C* and *B*, one of the S═O bonds is basically in the plane of the
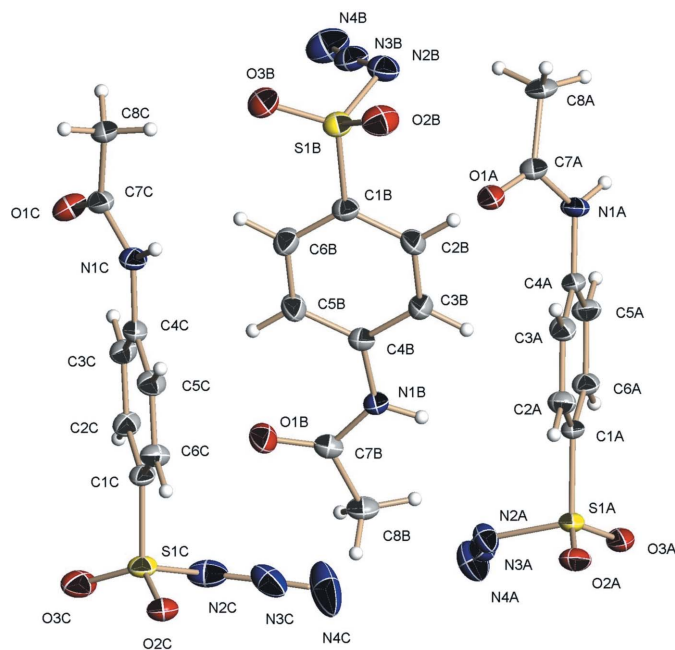
**Figure 1**
View of the three independent molecules of (I), showing 50% probability displacement ellipsoids.

six-membered ring, but for molecule A, the two S=O bonds are rotated out of this plane by 13.1 (2) and 31.31 (2)° (see Table 1 for a more exhaustive list of torsion angles). The tilt of the amide units also varies significantly. For molecule B, it is 9.77 (10)°, thus allowing for significant overlap between the π orbitals of the aromatic ring and the amide group. This is significantly diminished for molecule C, with a tilt angle of 18.65 (9)°, and for molecule A, with a tilt angle of 32.99 (8)°, it has to be assumed that the π overlap and delocalization is even less pronounced.

The loss of delocalization energy seems to be compensated for by the formation of hydrogen bonds between the amide units of all three molecules (Fig. 2 and Table 2). The hydrogen bonds observed here are in the usual range for strong amide-to-amide hydrogen bonds, and, as is often observed for amides and formamides and other related systems, the ability to form strong hydrogen bonds is the determining factor behind the type of packing realised in the solid state (Zeller *et al.*, 2005). For *p*-ABSA, the hydrogen bonds connect all three molecules, forming an infinite chain arranged in a helix-like fashion around the direction of the *b* axis of the unit cell (Fig. 2). This type of hydrogen-bonding interaction also allows molecules A and C to pair up to form π-stacked dimers with a centroid-to-centroid distance of 3.781 (1) Å, thus further energetically favouring the complicated molecular packing observed for *p*-ABSA (symmetry code for molecule C: $1 - x, -\frac{1}{2} + y, 1 - z$).

## Experimental

Compound (I) was purchased from Aldrich Chemicals and single crystals were grown from a solution in ethanol as large colourless blocks by slow evaporation of the solvent.

**Table 1**
Selected geometric parameters (Å, °).

| | | | |
|---|---|---|---|
| C7A—O1A | 1.232 (3) | N3B—N4B | 1.129 (3) |
| C7A—N1A | 1.363 (3) | N2C—N3C | 1.246 (4) |
| C7B—O1B | 1.220 (3) | N2C—S1C | 1.695 (2) |
| C7B—N1B | 1.360 (3) | N3C—N4C | 1.112 (4) |
| C7C—O1C | 1.217 (3) | O2A—S1A | 1.4266 (17) |
| C7C—N1C | 1.369 (3) | O3A—S1A | 1.4287 (18) |
| N2A—N3A | 1.244 (3) | O2B—S1B | 1.4266 (18) |
| N2A—S1A | 1.7034 (19) | O3B—S1B | 1.4320 (18) |
| N3A—N4A | 1.125 (3) | O2C—S1C | 1.4284 (16) |
| N2B—N3B | 1.251 (3) | O3C—S1C | 1.4217 (18) |
| N2B—S1B | 1.706 (2) | | |
| | | | |
| N3A—N2A—S1A | 112.86 (15) | N4B—N3B—N2B | 173.5 (3) |
| N4A—N3A—N2A | 173.8 (2) | N3C—N2C—S1C | 112.69 (18) |
| N3B—N2B—S1B | 112.81 (17) | N4C—N3C—N2C | 174.1 (3) |
| | | | |
| C2A—C1A—S1A—O2A | −13.1 (2) | C6B—C1B—S1B—O3B | 6.3 (2) |
| C6A—C1A—S1A—O3A | 31.31 (19) | C2C—C1C—S1C—O3C | −48.4 (2) |
| C2B—C1B—S1B—O2B | −40.0 (2) | C6C—C1C—S1C—O2C | −5.1 (2) |

**Table 2**
Hydrogen-bond geometry (Å, °).

| $D$—H···$A$ | $D$—H | H···$A$ | $D$···$A$ | $D$—H···$A$ |
|---|---|---|---|---|
| N1B—H1B···O1A$^i$ | 0.88 | 2.06 | 2.913 (2) | 162 |
| N1A—H1A···O1C$^{ii}$ | 0.88 | 2.03 | 2.907 (2) | 172 |
| N1C—H1C···O1B$^{iii}$ | 0.88 | 2.07 | 2.929 (2) | 165 |

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

Partial inversion twinning is present in the crystal which was examined; the Flack parameter (Flack, 1983) refined to 0.33 (4). All H atoms were placed in calculated positions (N—H = 0.88Å and C—H = 0.95–0.98Å). They were refined with isotropic displacement parameters of 1.5 (methyl) or 1.2 (all others) times that of the
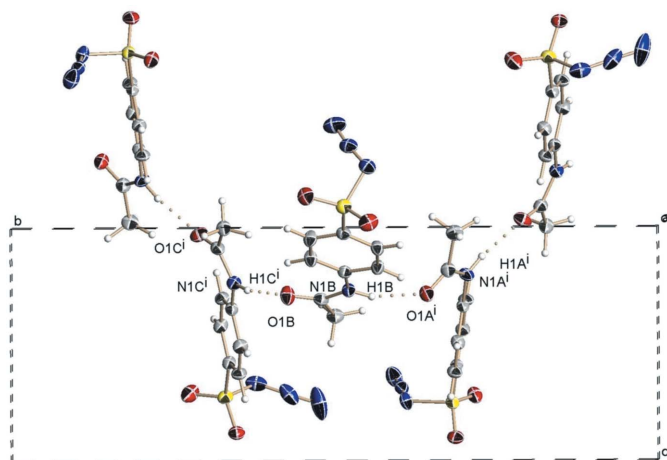
**Figure 2**
View along the *a* axis of (I), showing the hydrogen-bonding interactions as dotted lines. The molecules form an infinite hydrogen-bonded helix around the *b* axis of the unit cell. Displacement ellipsoids are drawn at the 50% probability level. [Symmetry code: (i) $x - 1$, $y$, $z$.]

equivalent isotropic displacement parameter of the parent C or N atom. Methyl H atoms were allowed to rotate to best fit the observed electron density. The s.u. values of the cell parameters are taken from the software, recognizing that the values are unreasonably small (Herbstein, 2000).

Data collection: *SMART* (Bruker, 2002); cell refinement: *SAINT-Plus* (Bruker, 2003); data reduction: *SAINT-Plus*; program(s) used to solve structure: *SHELXTL* (Bruker, 2000); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

## References

Baum, J. S., Shook, D. A., Davies, H. M. L. & Smith, H. D. (1987). *Synth. Commun.* **17**, 1709–1716.
Bruker (2000). *SHELXTL*. Version 6.14. Bruker AXS Inc, Madison, Wisconsin, USA.
Bruker (2002). *SMART for WNT/2000*. Version 5.630. Bruker AXS Inc, Madison, Wisconsin, USA.
Bruker (2003). *SAINT-Plus*. Version 6.45. Bruker AXS Inc, Madison, Wisconsin, USA.
Davies, H. M. L., Smith, H. D. & Korkor, O. (1987). *Tetrahedron Lett.* **28**, 1853–1856.
Flack, H. D. (1983). *Acta Cryst.* A**39**, 876–881.
Herbstein, F. H. (2000). *Acta Cryst.* B**56**, 547–557.
Taber, D. F., Sheth, R. B. & Joshi, P. V. (2005). *J. Org. Chem.* **70**, 2851–2854.
Zeller, M., Wilcox, R. J., Snyder, F. G., Seibel, H. A., Takas, N. J. & Hunter, A. D. (2005). *J. Chem. Crystallogr.* **35**, 723–729.