

1-(4-Methylphenylsulfonyl)-1*H*-1,2,3-benzotriazole: sheets built from C—H···N, C—H···O and C—H··· π (arene) hydrogen bonds**Ricaurte Rodríguez,^a Manuel Noguera,^a Justo Cobo,^a John N. Low^b and Christopher Glidewell^{c*}**^aDepartamento de Química Inorgánica y Orgánica, Universidad de Jaén, 23071 Jaén, Spain, ^bDepartment of Chemistry, University of Aberdeen, Meston Walk, Old Aberdeen AB24 3UE, Scotland, and ^cSchool of Chemistry, University of St Andrews, Fife KY16 9ST, Scotland

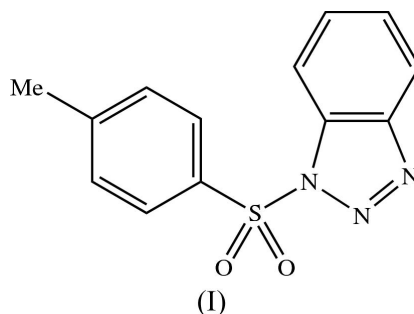
Correspondence e-mail: cg@st-andrews.ac.uk

Key indicatorsSingle-crystal X-ray study
 $T = 120$ K
Mean $\sigma(\text{C}-\text{C}) = 0.002$ Å
 R factor = 0.037
 wR factor = 0.098
Data-to-parameter ratio = 16.3For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

The molecules of the title compound, $\text{C}_{13}\text{H}_{11}\text{N}_3\text{O}_2\text{S}$, are linked into chains of edge-fused rings by a combination of C—H···N and C—H···O hydrogen bonds, and these chains are linked into sheets by a combination of a C—H··· π (arene) hydrogen bond and a second, rather weak, C—H···O hydrogen bond.

Comment

Sulfonylbenzotriazole derivatives are versatile synthetic intermediates both as benzotriazolyl donors (Katritzky *et al.*, 2001) and as sulfonyl donors (Katritzky *et al.*, 2004) because both have good leaving groups. The sulfonylbenzotriazoles can be readily prepared from benzotriazole and sulfonyl chlorides or from 1-chlorobenzotriazole and sulfonic acids. We report here the structure of 1-(4-methylphenylsulfonyl)-1*H*-1,2,3-benzotriazole, (I), which was obtained adventitiously in 54% yield when the addition of benzotriazole to the double bond in (4*S*,5*R*,6*R*)-diphenylmethyl (*E*)-4,5,6,7-tetrahydroxy-2-heptenoate was attempted in the presence of 4-toluenesulfonic acid. The direct reaction between benzotriazole and 4-toluenesulfonic acid in ethanol under reflux did not give any product and addition of diphenylmethanol to such a mixture yielded only the reported 1-diphenylmethyl-benzotriazole (Märky *et al.*, 1979), suggesting that transesterification, *via* a sulfonic ester, is required to produce the title compound in this way.



Within the molecules of (I), the bond distances (Table 1) show some evidence for modest bond fixation in the carbocyclic ring of the benzotriazole unit. Thus, the bonds C4—C5 and C6—C7 are significantly shorter than the bonds C3A—C4, C5—C6 and C7—C7A; the cross-ring bond C3A—C7A, expected to be the longest bond in this ring is, in fact, one of the shorter bonds. By contrast with this ring, the C—C distances in the benzenesulfonyl ring span the rather narrow range 1.386 (2)–1.395 (2) Å. There is clear bond fixation within the triazole ring. The exocyclic angles at the planar-configuration atom N1 differ by *ca* 10° and the O—S—O angle in the sulfonyl group is, as usually found in such fragments, much larger than the ideal tetrahedral value.

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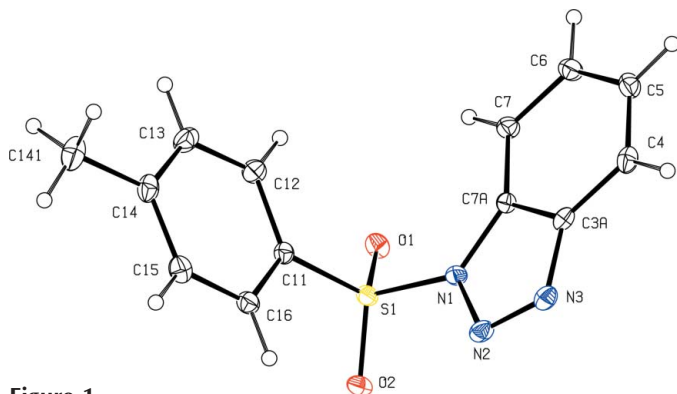


Figure 1
The molecule of compound (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level.

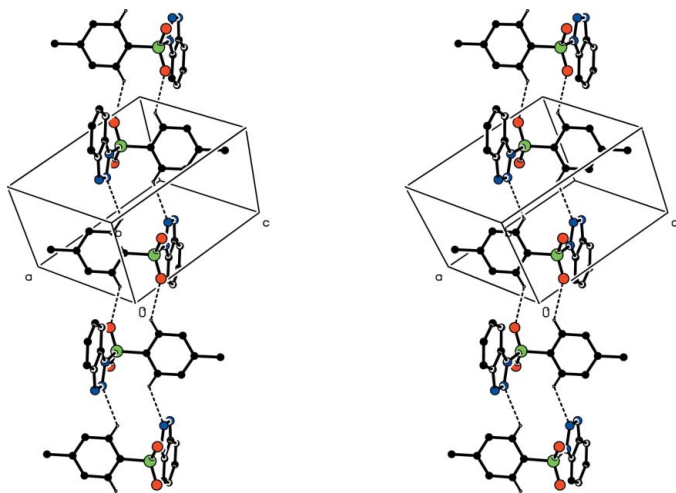


Figure 2
Stereoscopic view of part of the crystal structure of compound (I), showing the formation of a hydrogen-bonded chain along [111] containing two types of centrosymmetric $R_2^2(8)$ ring. For the sake of clarity, the H atoms not involved in the motifs shown have been omitted.

The molecules of (I) are linked by one C—H...N and one C—H...O hydrogen bond (Table 2) into chains of edge-fused rings. Aryl atom C16 in the molecule at (x, y, z) acts as hydrogen-bond donor to atom N2 in the molecule at $(1 - x, 1 - y, 1 - z)$, so generating a centrosymmetric $R_2^2(8)$ motif (Bernstein *et al.*, 1995); in addition, atom C12 at (x, y, z) acts as donor to atom O1 in the molecule at $(-x, -y, -z)$, thus generating a second centrosymmetric $R_2^2(8)$ motif. The combination of these two motifs then generates a chain of edge-fused rings running parallel to the [111] direction with the rings built from C—H...N hydrogen bonds centred at $(n + 0.5, n + 0.5, n + 0.5)$ ($n = \text{zero or integer}$) and the rings built from C—H...O hydrogen bonds centred at (n, n, n) ($n = \text{zero or integer}$) (Fig. 2).

Two further, but weaker, hydrogen bonds (Table 2) act cooperatively to link the [111] chains into sheets. Benzotriazole atoms C6 and C4 in the molecule at (x, y, z) act as hydrogen-bond donors, respectively, to atom O2 in the molecule at $(x, -1 + y, z)$ and to aryl ring C11–C16 in the molecule at $(1 - x, -y, 1 - z)$, both of which lie in a [111] chain offset from the reference chain by a unit translation along [010] (Fig. 3).

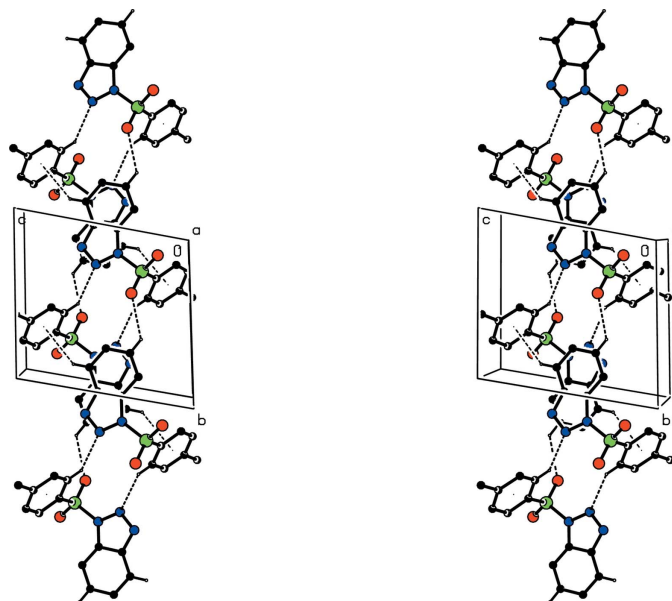


Figure 3
Stereoscopic view of part of the crystal structure of compound (I), showing the formation of a hydrogen-bonded chain along [010]. For the sake of clarity, the H atoms not involved in the motifs shown have been omitted.

Propagation by inversion of these hydrogen bonds then links [111] chains into $(10\bar{1})$ sheets, but there are no direction-specific interactions between adjacent sheets.

Experimental

A solution of (4*S*,5*R*,6*R*)-diphenylmethyl (*E*)-4,5,6,7-tetrahydroxy-2-heptenoate (0.15 g, 0.418 mmol), benzotriazole (0.05 g, 0.4 mmol) and 4-toluenesulfonic acid monohydrate (0.078 g, 0.41 mmol) in ethanol (20 ml) was heated under reflux for 45 min. The reaction mixture was cooled and then neutralized with saturated aqueous sodium carbonate solution; this neutralized mixture was then extracted with diethyl ether (2×10 ml). The organic extract was dried with sodium sulfate and the solvent was removed under reduced pressure to give the title compound in 54% yield (m.p. 407–409 K). Crystals suitable for single-crystal X-ray diffraction were grown from a solution in diethyl ether.

Crystal data

$C_{13}H_{11}N_3O_2S$	$Z = 2$
$M_r = 273.31$	$D_x = 1.469 \text{ Mg m}^{-3}$
Triclinic, $P\bar{1}$	Mo $K\alpha$ radiation
$a = 7.4211(3) \text{ \AA}$	Cell parameters from 2825 reflections
$b = 9.2176(3) \text{ \AA}$	$\theta = 4.1\text{--}27.5^\circ$
$c = 9.7823(3) \text{ \AA}$	$\mu = 0.26 \text{ mm}^{-1}$
$\alpha = 98.614(3)^\circ$	$T = 120(2) \text{ K}$
$\beta = 104.249(2)^\circ$	Needle, colourless
$\gamma = 102.684(3)^\circ$	$0.42 \times 0.18 \times 0.13 \text{ mm}$
$V = 617.87(4) \text{ \AA}^3$	

Data collection

Bruker–Nonius KappaCCD diffractometer	2825 independent reflections
φ and ω scans	2398 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (SADABS; Sheldrick, 2003)	$R_{\text{int}} = 0.036$
$T_{\text{min}} = 0.931, T_{\text{max}} = 0.967$	$\theta_{\text{max}} = 27.5^\circ$
14360 measured reflections	$h = -9 \rightarrow 9$
	$k = -11 \rightarrow 11$
	$l = -12 \rightarrow 12$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0482P)^2 + 0.2971P]$
$R[F^2 > 2\sigma(F^2)] = 0.037$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.098$	$(\Delta/\sigma)_{\max} < 0.001$
$S = 1.05$	$\Delta\rho_{\max} = 0.31 \text{ e } \text{Å}^{-3}$
2825 reflections	$\Delta\rho_{\min} = -0.48 \text{ e } \text{Å}^{-3}$
173 parameters	
H-atom parameters constrained	

Table 1

Selected geometric parameters (Å, °).

N1–N2	1.390 (2)	C3A–C4	1.402 (2)
N2–N3	1.288 (2)	C4–C5	1.375 (2)
N3–C3A	1.387 (2)	C5–C6	1.407 (2)
C3A–C7A	1.394 (2)	C6–C7	1.382 (2)
C7A–N1	1.3821 (19)	C7–C7A	1.396 (2)
N2–N1–S1	119.98 (10)	N2–N1–C7A	109.89 (12)
C7A–N1–S1	129.49 (11)	O1–S1–O2	121.89 (7)

Table 2

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
C4–H4 \cdots Cg1 ⁱ	0.95	2.84	3.641 (2)	143
C6–H6 \cdots O2 ⁱⁱ	0.95	2.59	3.247 (2)	127
C12–H12 \cdots O1 ⁱⁱⁱ	0.95	2.48	3.244 (2)	137
C16–H16 \cdots N2 ^{iv}	0.95	2.62	3.299 (2)	129

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

All H atoms were located from difference maps and then treated as riding atoms, with C–H = 0.95 (aromatic) or 0.98 Å (methyl) and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ or $1.5U_{\text{eq}}(\text{methyl C})$.

Data collection: *COLLECT* (Hooft, 1999); cell refinement: *DENZO* (Otwinowski & Minor, 1997) and *COLLECT*; data reduction: *DENZO* and *COLLECT*; program(s) used to solve structure: *OSCAIL* (McArdle, 2003) and *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *OSCAIL* and *SHELXL97* (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2003); software used to prepare material for publication: *SHELXL 97* and *PRPKAPPA* (Ferguson, 1999).

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