

1-Methanesulfonyl-1*H*-1,2,3-benzotriazole

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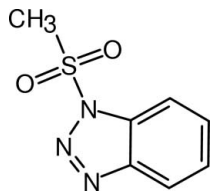
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 Key indicators: single-crystal X-ray study; $T = 150$ K; mean $\sigma(\text{C}-\text{C}) = 0.002$ Å; R factor = 0.030; wR factor = 0.082; data-to-parameter ratio = 15.8.

The molecular geometry of the title compound, $\text{C}_7\text{H}_7\text{N}_3\text{O}_2\text{S}$, does not differ much from that of the previously reported 4-toluenesulfonyl analogue. Unlike the latter compound, however, molecules of the title compound associate primarily *via* π - π stacking interactions of their benzene rings [centroid-centroid distance = 3.5865 (8) Å], forming columnar stacks along the crystallographic 2_1 axes. These stacks are interconnected *via* weak C—H \cdots O and C—H \cdots N hydrogen bonds.

Related literature

For crystal structure of 1-(*p*-toluenesulfonyl)-1*H*-1,2,3-benzotriazole, see: Rodríguez *et al.* (2005). For the preparation of the title compound and examples of its synthetic use, see: Katritzky *et al.* (1992, 2000).



Experimental

Crystal data

 $\text{C}_7\text{H}_7\text{N}_3\text{O}_2\text{S}$
 $M_r = 197.22$
 Monoclinic, $P2_1/c$
 $a = 9.3685$ (3) Å

 $b = 7.0627$ (2) Å
 $c = 12.4994$ (3) Å
 $\beta = 92.984$ (2)°
 $V = 825.93$ (4) Å³
 $Z = 4$
 Mo $K\alpha$ radiation
 $\mu = 0.36$ mm⁻¹
 $T = 150$ K
 $0.50 \times 0.30 \times 0.25$ mm

Data collection

 Nonius KappaCCD diffractometer
 14989 measured reflections
 1886 independent reflections

 1674 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.023$

Refinement

 $R[F^2 > 2\sigma(F^2)] = 0.030$
 $wR(F^2) = 0.082$
 $S = 1.09$
 1886 reflections

 119 parameters
 H-atom parameters constrained
 $\Delta\rho_{\text{max}} = 0.29$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.42$ e Å⁻³
Table 1

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$\text{C5}-\text{H5}\cdots\text{O2}^{\text{i}}$	0.93	2.55	3.270 (2)	135
$\text{C6}-\text{H6}\cdots\text{O1}^{\text{ii}}$	0.93	2.55	3.451 (2)	164
$\text{C8}-\text{H8B}\cdots\text{N3}^{\text{iii}}$	0.96	2.61	3.446 (2)	145
$\text{C8}-\text{H8C}\cdots\text{O2}^{\text{iv}}$	0.96	2.40	3.325 (2)	161

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

Data collection: *COLLECT* (Nonius, 2000); cell refinement: *SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *DENZO* (Otwinowski & Minor, 1997) and *SCALEPACK*; program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *PLATON* (Spek, 2009); software used to prepare material for publication: *PLATON*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: IM2237).

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supplementary materials

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1-Methanesulfonyl-1*H*-1,2,3-benzotriazole

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Comment

The title compound, 1-(methanesulfonyl)-1*H*-1,2,3-benzotriazole, is a useful and readily accessible organic reagent, acting as a convenient source of the benzotriazolyl anion. For instance, it reacts smoothly with carboxylic acids in the presence of a base to afford the corresponding 1-acyl-1*H*-1,2,3-benzotriazoles, which can be subsequently converted to amides in typically good yields (Katritzky *et al.*, 2000).

The molecular structure of the title compound (Fig. 1) is rather unexceptional, particularly in view of the geometric data reported earlier for the related 1*H*-1,2,3-benzotriazole derivative, 1-(*p*-toluenesulfonyl)-1*H*-1,2,3-benzotriazole (Rodríguez *et al.*, 2005). The N—N bonds within the triazole ring clearly maintain their localized character (*cf.* N1—N2 = 1.389 (2) Å, N3—N2 = 1.288 (2) Å), which is, however, not reflected in the adjacent bonds. The lengths of the remaining in-ring bonds, N1—C7A, C7A—C3A and C3A—N3, differ by less than *ca* 0.006 Å, while all in-ring angles span a range of 103.5 (1)–109.9 (1)°. On the other hand, the variation in the analogous parameters describing the geometry of the annelating benzene ring is less pronounced (*cf.* C—C = 1.371 (2)–1.408 (2) Å, C—C—C = 115.5 (1)–122.7 (1)°).

The methanesulfonyl group binds to the triazole ring somewhat unsymmetrically, which is best demonstrated by the difference in the S—N1—N2 (120.12 (9)°) and S—N1—C7A (129.8 (1)°) angles. Moreover, it is angularly distorted: The bond angles around sulfur span a range of 103.43 (6)–120.31 (7)° with the N1—S—C8 and O1—S—O2 angles being the lower and upper limit, respectively. The remaining angles do not differ much in the pairs: N1—S—O(1/2) (*ca* 105°, difference *ca* 0.4°), C8—S1—O(1/2) (*ca* 110°, difference *ca* 1.2°). Indeed, such a variation in bond angles corresponds with distances to the sulfur atom (S—O1 1.425 (1), S—O2 1.419 (1), S—N1 1.692 (1), S—C8 1.744 (2) Å) as the most acute angle is associated with the shortest bonds.

In the crystal, molecules of the title compound assemble *via* π – π stacking interactions of their benzene rings (Fig. 2a). Since this interaction involves molecules related by the crystallographic 2_1 screw axes, it results in the formation of infinite columnar stacks in the direction of the crystallographic *b* axis. It is worth pointing out that the observed separation of the ring centroids [$Cg \cdots Cg$ ($-x, 1/2 + y, 1/2 - z$; 3.5865 (8) Å)] is slightly shorter than that reported for α -graphite (*ca* 3.65 Å), where, however, the rings are slipped by *ca* 1.42 Å. Finally, the neighboring columnar stacks are interlinked by soft C—H \cdots O and C—H \cdots N hydrogen bonds (Table 1) into a complicated three-dimensional array (Figs. 2b and 2c).

Experimental

The title compound was synthesized from 1*H*-1,2,3-benzotriazole and methanesulfonyl chloride as described in the literature with a yield of 91% (Katritzky *et al.*, 2000). Crystals suitable for X-ray diffraction analysis were obtained by crystallization from warm benzene.

Refinement

H-atoms were included in calculated positions and refined as riding atoms with fixed C—H distances [C—H = 0.96 Å for CH₃, and 0.93 Å for aromatic CH] and $U_{\text{iso}}(\text{H})$ assigned to $1.5U_{\text{eq}}(\text{C})$ (CH₃) or $1.2U_{\text{eq}}(\text{C})$ (aromatic CH) of their bonding carbon atom.

Figures

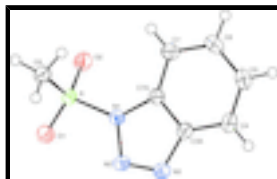


Fig. 1. Molecular structure of the title compound showing displacement ellipsoids for the non-H atoms at the 50% probability level. Hydrogen atoms are presented as spheres with arbitrary radii.

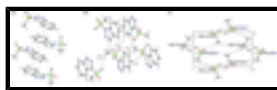


Fig. 2. (a) Section of columnar stacks connected by π - π interactions of the benzene rings [$Cg \cdots Cg = 3.5865(8)$ Å]. (b) H-bond interactions generated by the molecules of the title compounds. (c) View of the unit cell along the crystallographic a axis.

1-Methanesulfonyl-1H-1,2,3-benzotriazole

Crystal data

C₇H₇N₃O₂S

$M_r = 197.22$

Monoclinic, $P2_1/c$

Hall symbol: -P 2ybc

$a = 9.3685(3)$ Å

$b = 7.0627(2)$ Å

$c = 12.4994(3)$ Å

$\beta = 92.984(2)^\circ$

$V = 825.93(4)$ Å³

$Z = 4$

$F(000) = 408$

$D_x = 1.586$ Mg m⁻³

Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

Cell parameters from 2027 reflections

$\theta = 1.0$ – 27.5°

$\mu = 0.36$ mm⁻¹

$T = 150$ K

Block, colourless

$0.50 \times 0.30 \times 0.25$ mm

Data collection

Nonius KappaCCD
diffractometer

Radiation source: fine-focus sealed tube
horizontally mounted graphite crystal

Detector resolution: 9.091 pixels mm⁻¹
 ω and π scans to fill the Ewald sphere

14989 measured reflections

1886 independent reflections

1674 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.023$

$\theta_{\text{max}} = 27.5^\circ$, $\theta_{\text{min}} = 2.2^\circ$

$h = -12 \rightarrow 12$

$k = -9 \rightarrow 9$

$l = -16 \rightarrow 16$

Refinement

Refinement on F^2	Primary atom site location: structure-invariant direct methods
Least-squares matrix: full	Secondary atom site location: difference Fourier map
$R[F^2 > 2\sigma(F^2)] = 0.030$	Hydrogen site location: inferred from neighbouring sites
$wR(F^2) = 0.082$	H-atom parameters constrained
$S = 1.09$	$w = 1/[\sigma^2(F_o^2) + (0.0431P)^2 + 0.2983P]$
1886 reflections	where $P = (F_o^2 + 2F_c^2)/3$
119 parameters	$(\Delta/\sigma)_{\max} < 0.001$
0 restraints	$\Delta\rho_{\max} = 0.29 \text{ e } \text{\AA}^{-3}$
	$\Delta\rho_{\min} = -0.42 \text{ e } \text{\AA}^{-3}$

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two least-squares planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving least-squares planes.

Refinement. Refinement of F^2 against all diffractions. The weighted R -factor wR and goodness of fit S are based on F^2 , conventional R -factors R are based on F , with F set to zero for negative F^2 . The threshold expression of $F^2 > 2\sigma(F^2)$ is used only for calculating R -factors(gt) *etc.* and is not relevant to the choice of reflections for refinement. R -factors based on F^2 are statistically about twice as large as those based on F , and R -factors based on all data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
S	0.39056 (3)	0.07483 (5)	0.36695 (2)	0.02263 (12)
O1	0.32920 (11)	-0.04099 (16)	0.44586 (8)	0.0318 (3)
O2	0.51042 (11)	0.01011 (18)	0.31253 (8)	0.0337 (3)
N1	0.25880 (13)	0.10614 (17)	0.27080 (9)	0.0236 (3)
N2	0.29032 (13)	0.10541 (18)	0.16344 (9)	0.0274 (3)
N3	0.17185 (13)	0.11648 (19)	0.10673 (9)	0.0289 (3)
C3A	0.05897 (15)	0.1243 (2)	0.17395 (11)	0.0233 (3)
C4	-0.08866 (16)	0.1336 (2)	0.14889 (12)	0.0290 (3)
H4	-0.1253	0.1381	0.0784	0.035*
C5	-0.17615 (16)	0.1359 (2)	0.23349 (12)	0.0295 (3)
H5	-0.2746	0.1413	0.2200	0.035*
C6	-0.12050 (16)	0.1302 (2)	0.34029 (12)	0.0290 (3)
H6	-0.1837	0.1318	0.3953	0.035*
C7	0.02458 (16)	0.1222 (2)	0.36641 (11)	0.0273 (3)
H7	0.0611	0.1199	0.4370	0.033*
C7A	0.11237 (14)	0.11801 (19)	0.27980 (11)	0.0218 (3)
C8	0.41970 (16)	0.3025 (2)	0.41766 (11)	0.0277 (3)
H8A	0.4901	0.2977	0.4762	0.042*

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H8B	0.3319	0.3521	0.4424	0.042*
H8C	0.4531	0.3828	0.3623	0.042*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S	0.02097 (19)	0.0276 (2)	0.01921 (18)	0.00087 (12)	0.00002 (12)	0.00117 (12)
O1	0.0327 (6)	0.0361 (6)	0.0263 (5)	-0.0063 (5)	-0.0026 (4)	0.0100 (4)
O2	0.0245 (5)	0.0461 (7)	0.0306 (5)	0.0088 (5)	0.0010 (4)	-0.0071 (5)
N1	0.0209 (6)	0.0317 (6)	0.0183 (5)	0.0002 (5)	0.0016 (4)	0.0007 (4)
N2	0.0275 (6)	0.0369 (7)	0.0180 (5)	-0.0017 (5)	0.0030 (4)	0.0007 (5)
N3	0.0264 (6)	0.0402 (7)	0.0201 (6)	-0.0023 (5)	0.0002 (5)	0.0017 (5)
C3A	0.0252 (7)	0.0222 (7)	0.0223 (6)	-0.0016 (5)	-0.0002 (5)	0.0008 (5)
C4	0.0266 (7)	0.0293 (7)	0.0304 (7)	-0.0015 (6)	-0.0052 (6)	0.0009 (6)
C5	0.0220 (7)	0.0251 (7)	0.0413 (8)	-0.0012 (6)	0.0005 (6)	0.0008 (6)
C6	0.0263 (7)	0.0262 (7)	0.0352 (8)	0.0000 (6)	0.0100 (6)	0.0008 (6)
C7	0.0290 (7)	0.0294 (7)	0.0238 (7)	0.0010 (6)	0.0038 (5)	0.0010 (6)
C7A	0.0212 (6)	0.0217 (6)	0.0225 (6)	0.0001 (5)	0.0005 (5)	0.0006 (5)
C8	0.0301 (7)	0.0290 (7)	0.0239 (6)	-0.0017 (6)	0.0001 (5)	-0.0003 (6)

Geometric parameters (\AA , $^\circ$)

S—O2	1.4185 (10)	C4—H4	0.9300
S—O1	1.4254 (11)	C5—C6	1.408 (2)
S—N1	1.6919 (12)	C5—H5	0.9300
S—C8	1.7444 (15)	C6—C7	1.382 (2)
N1—C7A	1.3848 (17)	C6—H6	0.9300
N1—N2	1.3890 (16)	C7—C7A	1.3936 (19)
N2—N3	1.2878 (17)	C7—H7	0.9300
N3—C3A	1.3856 (18)	C8—H8A	0.9600
C3A—C7A	1.3905 (18)	C8—H8B	0.9600
C3A—C4	1.4037 (19)	C8—H8C	0.9600
C4—C5	1.371 (2)		
O2—S—O1	120.31 (7)	C4—C5—H5	119.2
O2—S—N1	105.55 (6)	C6—C5—H5	119.2
O1—S—N1	105.13 (6)	C7—C6—C5	122.41 (14)
O2—S—C8	111.01 (7)	C7—C6—H6	118.8
O1—S—C8	109.79 (7)	C5—C6—H6	118.8
N1—S—C8	103.43 (6)	C6—C7—C7A	115.48 (13)
C7A—N1—N2	109.87 (11)	C6—C7—H7	122.3
C7A—N1—S	129.75 (9)	C7A—C7—H7	122.3
N2—N1—S	120.12 (9)	N1—C7A—C3A	103.50 (11)
N3—N2—N1	108.12 (11)	N1—C7A—C7	133.75 (13)
N2—N3—C3A	109.37 (11)	C3A—C7A—C7	122.74 (13)
N3—C3A—C7A	109.12 (12)	S—C8—H8A	109.5
N3—C3A—C4	129.85 (13)	S—C8—H8B	109.5
C7A—C3A—C4	121.02 (13)	H8A—C8—H8B	109.5
C5—C4—C3A	116.74 (13)	S—C8—H8C	109.5

C5—C4—H4	121.6	H8A—C8—H8C	109.5
C3A—C4—H4	121.6	H8B—C8—H8C	109.5
C4—C5—C6	121.60 (14)		

Hydrogen-bond geometry (Å, °)

<i>D</i> —H \cdots <i>A</i>	<i>D</i> —H	H \cdots <i>A</i>	<i>D</i> \cdots <i>A</i>	<i>D</i> —H \cdots <i>A</i>
C5—H5 \cdots O2 ⁱ	0.93	2.55	3.270 (2)	135
C6—H6 \cdots O1 ⁱⁱ	0.93	2.55	3.451 (2)	164
C8—H8B \cdots N3 ⁱⁱⁱ	0.96	2.61	3.446 (2)	145
C8—H8C \cdots O2 ^{iv}	0.96	2.40	3.325 (2)	161

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

Fig. 1

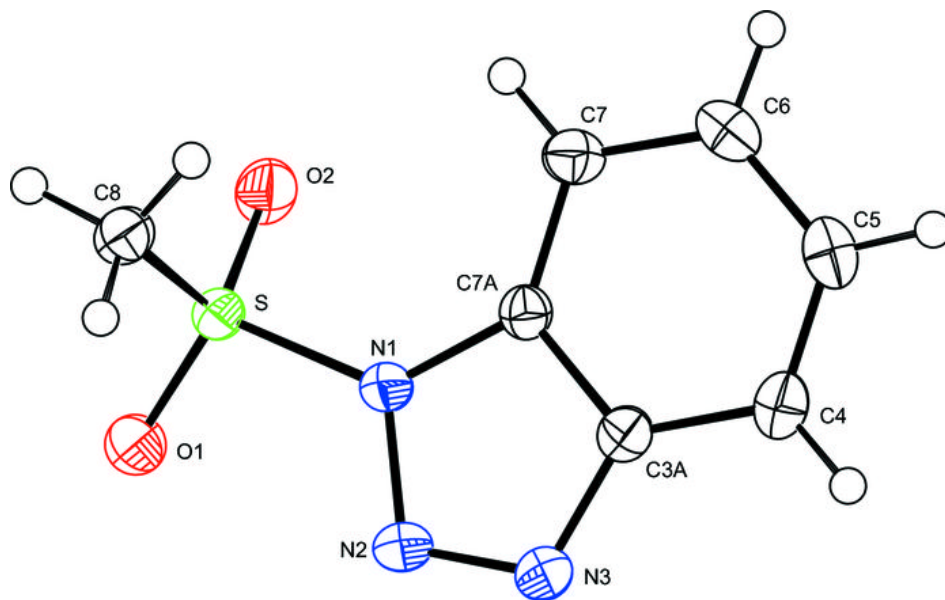


Fig. 2

