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3,5-Dinitrobenzyl methanesulfonate

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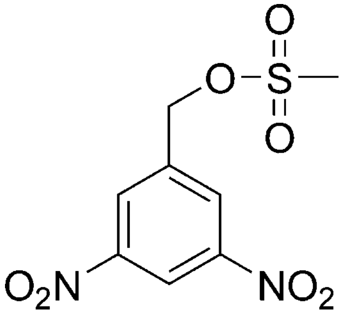
Key indicators: single-crystal X-ray study; T = 89 K; mean σ(C–C) = 0.002 Å; R factor = 0.033; wR factor = 0.088; data-to-parameter ratio = 13.7.

The title compound, $C_8H_8N_2O_7S$, an intermediate in the synthesis of N,N-bis(2-hydroxyethyl)-3,5-dinitroaniline, exists as a discrete molecule; the nitro groups are twisted with respect to the aromatic system [dihedral angles = 17.0 (1) and 26.3 (1)°].

Related literature

For the utility of benzyl methanesulfonates in synthesis, see: Barker *et al.* (2008); Bretonniere *et al.* (2004); Oh *et al.* (2004); Schirok *et al.* (2005). For the incorporation of N,N-bis(2-hydroxyethyl)benzylamines in macromolecular metal complexes, see: Crans & Boukhobza (1998); Koizumi *et al.* (2005, 2007).



Experimental

Crystal data

$C_8H_8N_2O_7S$
M_r = 276.22
Monoclinic, $P2_1/c$
a = 9.3549 (5) Å
b = 8.7552 (5) Å
c = 14.1526 (8) Å
β = 107.430 (1)°
V = 1105.91 (11) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.32 mm^{-1}
T = 89 (1) K
0.32 × 0.14 × 0.14 mm

Data collection

Bruker SMART diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1997)
$T_{\min}$ = 0.799, $T_{\max}$ = 0.971
6374 measured reflections
2233 independent reflections
1959 reflections with $I > 2\sigma(I)$
$R_{\rm int}$ = 0.019

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.033
$wR(F^2)$ = 0.088
S = 1.06
2233 reflections
163 parameters
H-atom parameters constrained
$\Delta\rho_{\max}$ = 0.28 e Å^{-3}
$\Delta\rho_{\min}$ = −0.49 e Å^{-3}

Data collection: *SMART* (Bruker, 1995); cell refinement: *SAINT* (Bruker, 1995); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEPIII* (Burnett & Johnson, 1996); software used to prepare material for publication: *SHELXTL* (Sheldrick, 2008).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: NG2470).

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supporting information

Acta Cryst. (2008). E**64**, o1470 [doi:10.1107/S1600536808020850]

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S1. Comment

Benzylic methansulfonates are readily prepared from benzylic alcohols and are often more easily prepared and more stable than the corresponding benzylic halide (Barker *et al.*, 2008). In particular benzylic methanesulfonates are useful for the preparation of *N*,*N*-bis(2-hydroxyethyl)benzylamines, which are nitrogen mustard precursors. The dual functionality of the two free hydroxyl groups along with a basic nitrogen have also seen *N*,*N*-bis(2-hydroxyethyl)benzylamines used in synthesis of numerous metal complexes including those containing vanadium (Crans & Boukhobza, 1998), manganese (Koizumi *et al.*, 2005, 2007) and iron (Koizumi *et al.*, 2005). There are no hydrogen bonding or π - π interactions in the crystal. The closest intermolecular contacts are O3 ··· N1 of 2.83 Å, and a pair of O ··· O 3.32 Å contacts between sulfonate oxygen atoms.

S2. Experimental

To a solution of 3,5-dinitrobenzyl alcohol (1.5 g, 7.57 mmol) and triethylamine (1.58 ml, 11.35 mmol) in dry THF (15 ml) at 0°C, under an atmosphere of nitrogen, was added dropwise a solution of methanesulfonyl chloride (0.88 ml, 11.35 mmol) in dry THF (5 ml) and the resulting solution stirred at room temperature for 3 h. The solvent was removed *in vacuo* and the residue diluted with ethyl acetate (150 ml), washed with brine (50 ml), dried ($MgSO_4$) and the solvent removed *in vacuo* to afford the title compound (2 g, 96%) as a yellow solid which was recrystallized from ethyl acetate to give yellow crystals (m.p. 356–357 K) suitable for X-ray crystallography. IR νmax (NaCl)/cm^{-1} 3399, 1627, 1541, 1458, 1344. ^{1}H NMR (400 MHz, $CDCl_3$, δ, p.p.m.) 3.15 (3*H*, s, CH_3), 5.40 (2*H*, s, CH_2O), 8.60 (2*H*, br s, Ar—H), 9.05 (1*H*, br s, Ar—H). δ_C (100 MHz, $CDCl_3$, δ, p.p.m.) 38.6 (CH_3, CH_3), 67.4 (CH_2, CH_2O), 119.5 (CH, Ar—C), 128.2 (CH, Ar—C), 138.6 (CH, Ar—C), 149.1 (quat., Ar—C). MS *m/z* (EI) 276 (M^+, 1%), 197 (100), 181 (42), 134 (20). HRMS (EI) Found M^+ 276.00489, $C_8H_8N_2O_7S$ requires 276.00522.

S3. Refinement

Hydrogen atoms were placed in calculated positions and refined using the riding model [C—H 0.93–0.97 Å), with U_{iso}(H) = 1.2 or 1.5 times U_{eq}(C).

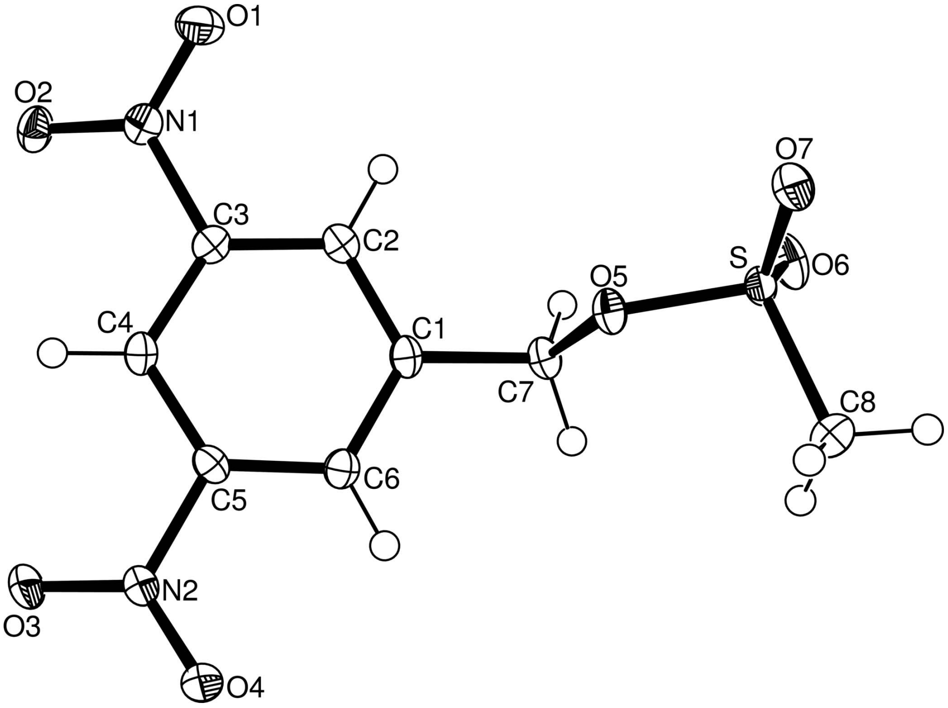

Figure 1

Structure showing 50% probability displacement ellipsoids for non-hydrogen atoms and hydrogen atoms as arbitary spheres (Burnett & Johnson, 1996).

3,5-Dinitrobenzyl methanesulfonate

Crystal data

$C_8H_8N_2O_7S$
M_r = 276.22
Monoclinic, $P2_1/c$
Hall symbol: -P 2ybc
a = 9.3549 (5) Å
b = 8.7552 (5) Å
c = 14.1526 (8) Å
β = 107.430 (1)°
V = 1105.91 (11) Å^3
Z = 4

$F(000)$ = 568
D_x = 1.659 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 4665 reflections
θ = 2.3–26.4°
μ = 0.32 mm^{-1}
T = 89 K
Rod, yellow
0.32 × 0.14 × 0.14 mm

Data collection

Bruker SMART diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1997)
$T_{\min}$ = 0.799, $T_{\max}$ = 0.971

6374 measured reflections
2233 independent reflections
1959 reflections with $I > 2\sigma(I)$
R_{int} = 0.019
$\theta_{\max}$ = 26.4°, $\theta_{\min}$ = 2.3°
$h = -9 \rightarrow 11$
$k = -10 \rightarrow 9$
$l = -17 \rightarrow 8$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.033$
$wR(F^2) = 0.088$
$S = 1.06$
2233 reflections
163 parameters
0 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0465P)^2 + 0.6248P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.28$ e Å^{-3}
$\Delta\rho_{min} = -0.49$ e Å^{-3}

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. 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 l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. 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 $F^2 > \sigma(F^2)$ 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 (Å^2)

	x	y	z	U_{iso}*/U_{eq}
S	0.28908 (4)	0.49088 (4)	0.39904 (3)	0.01554 (13)
O1	0.79782 (14)	0.02166 (15)	0.65112 (9)	0.0229 (3)
O2	0.75778 (13)	−0.16192 (14)	0.74420 (9)	0.0199 (3)
O3	0.23786 (14)	−0.34566 (14)	0.65950 (9)	0.0230 (3)
O4	0.06497 (14)	−0.21217 (16)	0.55662 (12)	0.0343 (4)
O5	0.31800 (13)	0.32888 (13)	0.45017 (8)	0.0171 (3)
O6	0.31513 (15)	0.60687 (14)	0.47320 (9)	0.0259 (3)
O7	0.37522 (14)	0.49312 (14)	0.33100 (9)	0.0223 (3)
N1	0.71506 (16)	−0.05791 (16)	0.68364 (10)	0.0166 (3)
N2	0.19482 (16)	−0.23139 (16)	0.60944 (11)	0.0191 (3)
C1	0.35300 (19)	0.15179 (18)	0.58246 (11)	0.0149 (3)
C2	0.50631 (18)	0.11998 (19)	0.61537 (11)	0.0155 (3)
H2A	0.5761	0.1957	0.6155	0.019*
C3	0.55267 (18)	−0.02626 (19)	0.64782 (12)	0.0148 (3)
C4	0.45474 (18)	−0.14488 (18)	0.64856 (11)	0.0148 (3)
H4A	0.4880	−0.2418	0.6720	0.018*
C5	0.30408 (18)	−0.10912 (18)	0.61204 (11)	0.0150 (3)
C6	0.25038 (19)	0.03509 (19)	0.57931 (12)	0.0154 (3)
H6A	0.1479	0.0536	0.5557	0.019*
C7	0.29970 (19)	0.31110 (18)	0.54971 (12)	0.0163 (3)
H7A	0.1955	0.3235	0.5470	0.020*
H7B	0.3593	0.3862	0.5951	0.020*
C8	0.0984 (2)	0.4858 (2)	0.33155 (17)	0.0319 (5)
H8A	0.0702	0.5810	0.2974	0.048*
H8B	0.0399	0.4696	0.3760	0.048*

H8C	0.0807	0.4040	0.2843	0.048*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S	0.0168 (2)	0.0125 (2)	0.0157 (2)	−0.00083 (14)	0.00236 (16)	0.00293 (14)
O1	0.0180 (6)	0.0286 (7)	0.0219 (7)	−0.0040 (5)	0.0057 (5)	0.0021 (5)
O2	0.0211 (6)	0.0168 (6)	0.0175 (6)	0.0029 (5)	−0.0006 (5)	0.0006 (5)
O3	0.0241 (7)	0.0172 (6)	0.0263 (7)	−0.0011 (5)	0.0057 (5)	0.0086 (5)
O4	0.0164 (7)	0.0248 (7)	0.0529 (9)	−0.0036 (5)	−0.0030 (6)	0.0140 (7)
O5	0.0237 (6)	0.0143 (6)	0.0134 (6)	0.0010 (5)	0.0055 (5)	0.0022 (4)
O6	0.0421 (8)	0.0133 (6)	0.0230 (6)	−0.0022 (5)	0.0105 (6)	0.0000 (5)
O7	0.0250 (7)	0.0227 (7)	0.0200 (6)	−0.0002 (5)	0.0079 (5)	0.0053 (5)
N1	0.0176 (7)	0.0164 (7)	0.0138 (6)	−0.0001 (6)	0.0018 (6)	−0.0035 (6)
N2	0.0189 (7)	0.0149 (7)	0.0227 (7)	−0.0007 (6)	0.0052 (6)	0.0035 (6)
C1	0.0207 (8)	0.0135 (8)	0.0100 (7)	0.0010 (6)	0.0038 (6)	0.0006 (6)
C2	0.0190 (8)	0.0147 (8)	0.0126 (7)	−0.0022 (6)	0.0044 (6)	−0.0009 (6)
C3	0.0155 (8)	0.0178 (8)	0.0099 (7)	0.0001 (6)	0.0018 (6)	−0.0016 (6)
C4	0.0200 (8)	0.0132 (8)	0.0101 (7)	0.0020 (6)	0.0030 (6)	0.0000 (6)
C5	0.0185 (8)	0.0140 (8)	0.0124 (7)	−0.0028 (6)	0.0046 (6)	−0.0004 (6)
C6	0.0171 (8)	0.0163 (8)	0.0120 (7)	0.0010 (6)	0.0031 (6)	0.0005 (6)
C7	0.0216 (8)	0.0136 (8)	0.0136 (8)	−0.0003 (6)	0.0053 (6)	0.0009 (6)
C8	0.0177 (9)	0.0331 (11)	0.0390 (12)	0.0005 (8)	−0.0002 (8)	0.0141 (9)

Geometric parameters (Å, º)

S—O6	1.4279 (13)	C1—C7	1.507 (2)
S—O7	1.4290 (13)	C2—C3	1.385 (2)
S—O5	1.5783 (12)	C2—H2A	0.9300
S—C8	1.7538 (19)	C3—C4	1.387 (2)
O1—N1	1.2289 (19)	C4—C5	1.384 (2)
O2—N1	1.2322 (18)	C4—H4A	0.9300
O3—N2	1.2223 (18)	C5—C6	1.386 (2)
O4—N2	1.2323 (19)	C6—H6A	0.9300
O5—C7	1.4773 (19)	C7—H7A	0.9700
N1—C3	1.476 (2)	C7—H7B	0.9700
N2—C5	1.473 (2)	C8—H8A	0.9600
C1—C6	1.394 (2)	C8—H8B	0.9600
C1—C2	1.397 (2)	C8—H8C	0.9600
O6—S—O7	118.62 (8)	C5—C4—C3	115.40 (15)
O6—S—O5	109.52 (7)	C5—C4—H4A	122.3
O7—S—O5	105.51 (7)	C3—C4—H4A	122.3
O6—S—C8	109.88 (10)	C4—C5—C6	123.88 (15)
O7—S—C8	108.68 (9)	C4—C5—N2	117.80 (14)
O5—S—C8	103.51 (8)	C6—C5—N2	118.32 (14)
C7—O5—S	118.62 (10)	C5—C6—C1	118.68 (15)
O1—N1—O2	124.75 (14)	C5—C6—H6A	120.7

O1—N1—C3	117.64 (13)	C1—C6—H6A	120.7
O2—N1—C3	117.61 (14)	O5—C7—C1	105.58 (13)
O3—N2—O4	123.85 (14)	O5—C7—H7A	110.6
O3—N2—C5	118.35 (13)	C1—C7—H7A	110.6
O4—N2—C5	117.80 (14)	O5—C7—H7B	110.6
C6—C1—C2	119.55 (15)	C1—C7—H7B	110.6
C6—C1—C7	120.50 (15)	H7A—C7—H7B	108.8
C2—C1—C7	119.95 (15)	S—C8—H8A	109.5
C3—C2—C1	118.88 (15)	S—C8—H8B	109.5
C3—C2—H2A	120.6	H8A—C8—H8B	109.5
C1—C2—H2A	120.6	S—C8—H8C	109.5
C2—C3—C4	123.55 (15)	H8A—C8—H8C	109.5
C2—C3—N1	118.36 (14)	H8B—C8—H8C	109.5
C4—C3—N1	118.09 (14)		