

3,5-Dinitrobenzyl methanesulfonate

Gul S. Khan, George R. Clark and David Barker*

Chemistry Department, The University of Auckland, Private Bag 92019, Auckland, New Zealand

Correspondence e-mail: g.clark@auckland.ac.nz

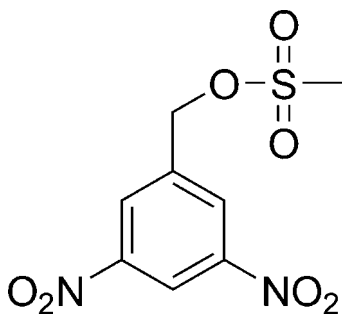
Received 1 July 2008; accepted 6 July 2008

 Key indicators: single-crystal X-ray study; $T = 89$ K; mean $\sigma(\text{C}-\text{C}) = 0.002$ Å; R factor = 0.033; wR factor = 0.088; data-to-parameter ratio = 13.7.

The title compound, $\text{C}_8\text{H}_8\text{N}_2\text{O}_7\text{S}$, 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

 $\text{C}_8\text{H}_8\text{N}_2\text{O}_7\text{S}$
 $M_r = 276.22$

 Monoclinic, $P2_1/c$
 $a = 9.3549$ (5) Å

 $b = 8.7552$ (5) Å

 $c = 14.1526$ (8) Å

 $\beta = 107.430$ (1)°

 $V = 1105.91$ (11) Å³
 $Z = 4$

 Mo $K\alpha$ radiation

 $\mu = 0.32$ mm⁻¹
 $T = 89$ (1) K

 $0.32 \times 0.14 \times 0.14$ 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 $I > 2\sigma(I)$
 $R_{\text{int}} = 0.019$

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

 $\Delta\rho_{\text{max}} = 0.28$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.49$ 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).

The authors acknowledge financial support from the Higher Education Commission of Pakistan and the University of Auckland, New Zealand.

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

References

- Barker, D., Lehmann, A. L., Mai, A., Khan, G. S. & Ng, E. (2008). *Tetrahedron Lett.* **49**, 1660–1664.
- Bretonniere, Y., Cann, M. J., Parker, D. & Slater, R. (2004). *Org. Biomol. Chem.* **2**, 1624–1632.
- Bruker (1995). SMART and SAINT Bruker AXS Inc., Madison, Wisconsin, USA.
- Burnett, M. N. & Johnson, C. K. (1996). ORTEPIII. Report ORNL-6895. Oak Ridge National Laboratory, Tennessee, USA.
- Crans, D. C. & Boukhobza, I. (1998). *J. Am. Chem. Soc.* **120**, 8069–8078.
- Koizumi, S., Nihei, M., Nakano, M. & Oshio, H. (2005). *Inorg. Chem.* **44**, 1208–1210.
- Koizumi, S., Nihei, M., Shiga, T., Nakano, M., Nojiri, H., Bircher, R., Waldmann, O., Ochsenbein, S. T., Guedel, H. U., Fernandez-Alonso, F. & Oshio, H. (2007). *Chem. Eur. J.* **13**, 8445–8453.
- Oh, S.-J., Lee, K. C., Lee, S.-Y., Ryu, E. K., Saji, H., Choe, Y. S., Chi, D. Y., Kim, S. E., Lee, J. & Kim, B.-T. (2004). *Bioorg. Med. Chem.* **12**, 5505–5513.
- Schirok, H., Alonso-Alija, C., Benet-Buchholz, J., Goeller, A. H., Grosser, R., Michels, M. & Paulsen, H. (2005). *J. Org. Chem.* **70**, 9463–9469.
- Sheldrick, G. M. (1997). SADABS. Univ. of Göttingen, Germany.
- Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.

supplementary materials

Acta Cryst. (2008). E64, o1470 [doi:10.1107/S1600536808020850]

3,5-Dinitrobenzyl methanesulfonate

G. S. Khan, G. R. Clark and D. Barker

Comment

Benzylic methanesulfonates 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 \cdots N1 of 2.83 Å, and a pair of O \cdots O 3.32 Å contacts between sulfonate oxygen atoms.

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 (MgSO₄) 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 ν_{\max} (NaCl)/cm⁻¹ 3399, 1627, 1541, 1458, 1344. ¹H NMR (400 MHz, CDCl₃, δ , p.p.m.) 3.15 (3H, s, CH₃), 5.40 (2H, s, CH₂O), 8.60 (2H, br s, Ar—H), 9.05 (1H, br s, Ar—H). δ_{C} (100 MHz, CDCl₃, δ , p.p.m.) 38.6 (CH₃, CH₃), 67.4 (CH₂, CH₂O), 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, C₈H₈N₂O₇S requires 276.00522.

Refinement

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

Figures

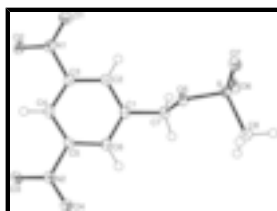


Fig. 1. : Structure showing 50% probability displacement ellipsoids for non-hydrogen atoms and hydrogen atoms as arbitrary spheres (Burnett & Johnson, 1996).

3,5-Dinitrobenzyl methanesulfonate

Crystal data

| | |
|----------------------------------|---|
| $C_8H_8N_2O_7S$ | $F_{000} = 568$ |
| $M_r = 276.22$ | $D_x = 1.659 \text{ Mg m}^{-3}$ |
| Monoclinic, $P2_1/c$ | Mo $K\alpha$ radiation |
| Hall symbol: -P 2ybc | $\lambda = 0.71073 \text{ \AA}$ |
| $a = 9.3549 (5) \text{ \AA}$ | Cell parameters from 4665 reflections |
| $b = 8.7552 (5) \text{ \AA}$ | $\theta = 2.3\text{--}26.4^\circ$ |
| $c = 14.1526 (8) \text{ \AA}$ | $\mu = 0.32 \text{ mm}^{-1}$ |
| $\beta = 107.430 (1)^\circ$ | $T = 89 (1) \text{ K}$ |
| $V = 1105.91 (11) \text{ \AA}^3$ | Rod, yellow |
| $Z = 4$ | $0.32 \times 0.14 \times 0.14 \text{ mm}$ |

Data collection

| | |
|---|--|
| Bruker SMART diffractometer | 2233 independent reflections |
| Radiation source: fine-focus sealed tube | 1959 reflections with $I > 2\sigma(I)$ |
| Monochromator: graphite | $R_{\text{int}} = 0.019$ |
| $T = 89(1) \text{ K}$ | $\theta_{\text{max}} = 26.4^\circ$ |
| ω scans | $\theta_{\text{min}} = 2.3^\circ$ |
| Absorption correction: multi-scan (SADABS; Sheldrick, 1997) | $h = -9 \rightarrow 11$ |
| $T_{\text{min}} = 0.799$, $T_{\text{max}} = 0.971$ | $k = -10 \rightarrow 9$ |
| 6374 measured reflections | $l = -17 \rightarrow 8$ |

Refinement

| | |
|--|--|
| Refinement on F^2 | Secondary atom site location: difference Fourier map |
| Least-squares matrix: full | Hydrogen site location: inferred from neighbouring sites |
| $R[F^2 > 2\sigma(F^2)] = 0.033$ | H-atom parameters constrained |
| $wR(F^2) = 0.088$ | $w = 1/[\sigma^2(F_o^2) + (0.0465P)^2 + 0.6248P]$ |
| $S = 1.06$ | where $P = (F_o^2 + 2F_c^2)/3$ |
| 2233 reflections | $(\Delta/\sigma)_{\text{max}} = 0.001$ |
| 163 parameters | $\Delta\rho_{\text{max}} = 0.28 \text{ e \AA}^{-3}$ |
| Primary atom site location: structure-invariant direct methods | $\Delta\rho_{\text{min}} = -0.49 \text{ e \AA}^{-3}$ |
| | Extinction correction: none |

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 (\AA^2)

| | <i>x</i> | <i>y</i> | <i>z</i> | $U_{\text{iso}}^*/U_{\text{eq}}$ |
|-----|--------------|---------------|--------------|----------------------------------|
| 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 (\AA^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) |

supplementary materials

| | | | | | | |
|----|------------|-------------|-------------|-------------|-------------|-------------|
| 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, °)

| | | | |
|----------|-------------|------------|-------------|
| 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) | | |

Fig. 1

