organic compounds

p-Tosylhydrazine: a redetermination from single-crystal data at 100 K

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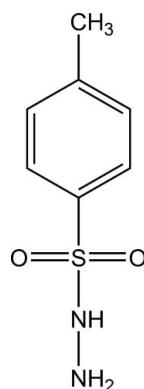Correspondence e-mail: ashwini_nangia@rediffmail.com

Redetermination of the structure of the title compound, alternatively called 4-methylbenzenesulfonohydrazide, $C_7H_{10}N_2O_2S$, at 100 K reveals that both H atoms of the NH_2 group form intermolecular N—H···O hydrogen bonds, which together with an N—H···O hydrogen bond from the NH group form a sheet-like structure in the ab plane.

Related literature

For a previous determination of the structure from powder X-ray diffraction data, see: Lightfoot *et al.* (1993). For the synthesis, see: Friedman *et al.* (1973).

Experimental

Crystal data

$C_7H_{10}N_2O_2S$	Monoclinic, $P2_1/c$
M_r = 186.23	a = 8.4166 (8) Å

b = 5.6056 (5) Å
c = 17.9484 (17) Å
β = 100.260 (1)°
V = 833.27 (13) Å^3
Z = 4

Mo $K\alpha$ radiation
μ = 0.35 mm^{-1}
T = 100 (2) K
$0.30 \times 0.18 \times 0.10$ mm

Data collection

Bruker APEX CCD diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2003)
T_{min} = 0.903, T_{max} = 0.966

8195 measured reflections
1641 independent reflections
1584 reflections with $I > 2\sigma(I)$
R_{int} = 0.034

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.060
$wR(F^2)$ = 0.117
S = 1.30
1641 reflections
122 parameters
1 restraint

H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.65 e Å^{-3}
$\Delta\rho_{min}$ = −0.31 e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1···O1^{i}	0.96 (2)	2.00 (2)	2.948 (3)	173 (3)
N2—H2A···O2^{ii}	0.86 (4)	2.28 (4)	3.122 (4)	167 (3)
N2—H2B···O2^{iii}	0.89 (4)	2.27 (4)	3.118 (3)	160 (3)

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

Data collection: *SMART* (Bruker, 1997); cell refinement: *SAINT* (Bruker, 1997); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 2000); software used to prepare material for publication: *SHELXTL* and *X-SEED* (Barbour, 2001).

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: BI2204).

References

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supplementary materials

p-Tosylhydrazine: a redetermination from single-crystal data at 100 K

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Comment

The structure of the title compound, $C_7H_{10}N_2O_2S$ (Figure 1), has been determined previously by Lightfoot *et al.* (1993) from powder X-ray diffraction data. However, H atoms could not be located using that technique and the authors assumed the presence of an intramolecular N—H⋯O hydrogen bond (graph-set motif S(5)). Re-determination of the structure using single-crystal X-ray diffraction reveals that the H atoms of the NH_2 group actually make intermolecular N—H⋯O hydrogen bonds, with O1 and O2 acting as acceptors (Table 1). The N1—H1⋯O1 and N2—H2A⋯O2 hydrogen bonds link the molecules into double chains along the *b* axis, and these chains are linked *via* N2—H2B⋯O2 hydrogen bonds to form a sheet-like structure in the *ab* planes.

Experimental

Single crystals of 4-tosylhydrazine (Friedman *et al.*, 1973) were obtained by recrystallization from ethanol.

Refinement

Atoms H2A and H2B of the NH_2 group were located in difference Fourier maps and refined isotropically without restraint. Atom H1 was also located in a difference Fourier map and refined with the N—H distance restrained to be 1.01 (2) Å. All other H atoms were visible in difference Fourier maps but were placed at calculated positions and allowed to ride with C—H = 0.95 Å and $U_{iso}(H) = 1.2U_{eq}(C)$ for aromatic H atoms, and with C—H = 0.98 Å and $U_{iso}(H) = 1.5U_{eq}(C)$ for methyl H atoms.
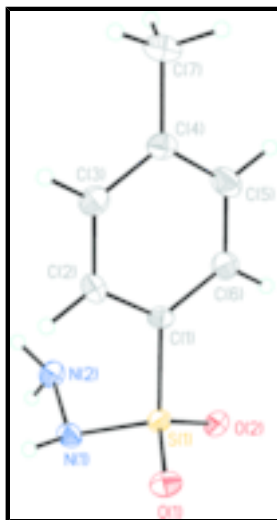
Figures

Fig. 1. Molecular structure of the title compound with displacement ellipsoids drawn at the 50% probability level for non-H atoms.
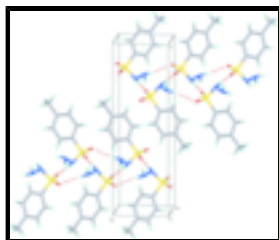
Fig. 2. N—H···O hydrogen bonds connect the molecules into double chains along the *b* axis.

4-Methylbenzenesulfonohydrazide

Crystal data

$C_7H_{10}N_2O_2S$	$F_{000} = 392$
$M_r = 186.23$	$D_x = 1.484$ Mg m^{-3}
Monoclinic, $P2_1/c$	Melting point: 382 K
Hall symbol: -P 2ybc	Mo $K\alpha$ radiation $\lambda = 0.71073$ Å
$a = 8.4166$ (8) Å	Cell parameters from 5282 reflections
$b = 5.6056$ (5) Å	$\theta = 2.3–26.0^\circ$
$c = 17.9484$ (17) Å	$\mu = 0.35$ mm^{-1}
$\beta = 100.260$ (1)$^\circ$	$T = 100$ (2) K
$V = 833.27$ (13) Å^3	Block, colourless
$Z = 4$	$0.30 \times 0.18 \times 0.10$ mm

Data collection

Bruker APEX CCD diffractometer	1641 independent reflections
Radiation source: fine-focus sealed tube	1584 reflections with $I > 2\sigma(I)$
Monochromator: graphite	$R_{int} = 0.034$
$T = 100(2)$ K	$\theta_{max} = 26.0^\circ$
φ and ω scans	$\theta_{min} = 2.3^\circ$
Absorption correction: multi-scan (SADABS; Sheldrick, 2003)	$h = -10 \rightarrow 10$
$T_{min} = 0.903$, $T_{max} = 0.966$	$k = -6 \rightarrow 6$
8195 measured reflections	$l = -22 \rightarrow 22$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.060$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.117$	$w = 1/[\sigma^2(F_o^2) + (0.0212P)^2 + 1.9226P]$ where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.30$	$(\Delta/\sigma)_{max} = 0.001$
1641 reflections	$\Delta\rho_{max} = 0.65$ e Å^{-3}

122 parameters	$\Delta\rho_{min} = -0.31$ e Å^{-3}
1 restraint	Extinction correction: none
Primary atom site location: structure-invariant direct methods	

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 > 2sigma(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}
S1	0.27606 (8)	0.14178 (13)	0.17916 (4)	0.0144 (2)
O1	0.4359 (2)	0.0492 (4)	0.20362 (12)	0.0207 (5)
O2	0.1440 (2)	−0.0239 (4)	0.16470 (12)	0.0184 (5)
N1	0.2469 (3)	0.3220 (5)	0.24704 (14)	0.0173 (6)
H1	0.346 (3)	0.402 (5)	0.2665 (17)	0.015 (8)*
N2	0.1052 (3)	0.4620 (5)	0.22597 (16)	0.0191 (6)
H2A	0.130 (4)	0.605 (7)	0.215 (2)	0.026 (10)*
H2B	0.056 (4)	0.467 (7)	0.266 (2)	0.027 (10)*
C1	0.2708 (3)	0.3161 (5)	0.09705 (16)	0.0149 (6)
C2	0.3625 (4)	0.5216 (6)	0.10103 (17)	0.0179 (6)
H2	0.4279	0.5681	0.1475	0.021*
C3	0.3581 (4)	0.6590 (6)	0.03662 (17)	0.0204 (7)
H3	0.4215	0.8001	0.0392	0.024*
C4	0.2624 (4)	0.5941 (6)	−0.03207 (17)	0.0182 (6)
C5	0.1721 (4)	0.3860 (6)	−0.03418 (18)	0.0252 (7)
H5	0.1070	0.3383	−0.0806	0.030*
C6	0.1747 (4)	0.2466 (6)	0.02964 (17)	0.0207 (7)
H6	0.1116	0.1053	0.0273	0.025*
C7	0.2553 (4)	0.7451 (7)	−0.10152 (18)	0.0256 (7)
H7A	0.2719	0.6444	−0.1441	0.038*
H7B	0.3400	0.8671	−0.0923	0.038*
H7C	0.1495	0.8225	−0.1136	0.038*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.0148 (4)	0.0132 (4)	0.0152 (4)	0.0006 (3)	0.0022 (3)	0.0006 (3)
O1	0.0182 (11)	0.0210 (11)	0.0221 (12)	0.0033 (9)	0.0017 (9)	0.0038 (9)

O2	0.0199 (11)	0.0146 (11)	0.0210 (11)	0.0003 (9)	0.0045 (9)	0.0008 (9)
C5	0.0239 (16)	0.0307 (19)	0.0185 (16)	0.0005 (14)	−0.0029 (13)	−0.0018 (14)
C1	0.0130 (13)	0.0165 (15)	0.0148 (14)	0.0025 (11)	0.0017 (11)	0.0025 (12)
N1	0.0162 (12)	0.0191 (14)	0.0159 (12)	−0.0016 (11)	0.0008 (10)	−0.0001 (10)
N2	0.0186 (13)	0.0181 (14)	0.0216 (14)	0.0017 (11)	0.0058 (11)	−0.0009 (12)
C2	0.0168 (14)	0.0209 (16)	0.0155 (14)	−0.0011 (12)	0.0015 (12)	−0.0037 (12)
C6	0.0198 (15)	0.0197 (16)	0.0213 (16)	−0.0022 (13)	−0.0002 (12)	−0.0004 (13)
C3	0.0197 (15)	0.0192 (16)	0.0229 (16)	−0.0009 (13)	0.0053 (12)	0.0015 (13)
C7	0.0247 (17)	0.0330 (19)	0.0193 (16)	0.0039 (15)	0.0042 (13)	0.0066 (14)
C4	0.0171 (14)	0.0201 (16)	0.0182 (15)	0.0070 (12)	0.0054 (12)	0.0022 (12)

Geometric parameters (Å, °)

S1—O1	1.436 (2)	N2—H2A	0.86 (4)
S1—O2	1.436 (2)	N2—H2B	0.89 (4)
S1—N1	1.635 (3)	C2—C3	1.384 (4)
S1—C1	1.762 (3)	C2—H2	0.950
C5—C6	1.384 (4)	C6—H6	0.950
C5—C4	1.389 (5)	C3—C4	1.395 (4)
C5—H5	0.950	C3—H3	0.950
C1—C2	1.381 (4)	C7—C4	1.499 (4)
C1—C6	1.386 (4)	C7—H7A	0.980
N1—N2	1.422 (4)	C7—H7B	0.980
N1—H1	0.96 (2)	C7—H7C	0.980
O1—S1—O2	118.33 (13)	C1—C2—C3	119.3 (3)
O1—S1—N1	104.61 (13)	C1—C2—H2	120.3
O2—S1—N1	108.68 (13)	C3—C2—H2	120.3
O1—S1—C1	109.81 (13)	C5—C6—C1	119.0 (3)
O2—S1—C1	107.70 (13)	C5—C6—H6	120.5
N1—S1—C1	107.22 (14)	C1—C6—H6	120.5
C6—C5—C4	121.6 (3)	C2—C3—C4	121.2 (3)
C6—C5—H5	119.2	C2—C3—H3	119.4
C4—C5—H5	119.2	C4—C3—H3	119.4
C2—C1—C6	120.9 (3)	C4—C7—H7A	109.5
C2—C1—S1	119.2 (2)	C4—C7—H7B	109.5
C6—C1—S1	119.9 (2)	H7A—C7—H7B	109.5
N2—N1—S1	111.91 (19)	C4—C7—H7C	109.5
N2—N1—H1	118 (2)	H7A—C7—H7C	109.5
S1—N1—H1	108.8 (19)	H7B—C7—H7C	109.5
N1—N2—H2A	110 (2)	C5—C4—C3	118.0 (3)
N1—N2—H2B	107 (2)	C5—C4—C7	120.7 (3)
H2A—N2—H2B	109 (3)	C3—C4—C7	121.3 (3)

Hydrogen-bond geometry (Å, °)

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1···O1[i]	0.96 (2)	2.00 (2)	2.948 (3)	173 (3)
N2—H2A···O2[ii]	0.86 (4)	2.28 (4)	3.122 (4)	167 (3)

N2—H2B···O2[iii]	0.89 (4)	2.27 (4)	3.118 (3)	160 (3)

Symmetry codes: (i) −*x*+1, *y*+1/2, −*z*+1/2; (ii) *x*, *y*+1, *z*; (iii) −*x*, *y*+1/2, −*z*+1/2.

Fig. 1

Fig. 2