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N-Methyl-3-methylsulfonyl-*N*-nitroaniline

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In the title compound, $C_8H_{10}N_2O_4S$, the N—N bond length [1.3488 (18) Å] indicates some double-bond character, while the torsion angle between the aromatic ring and the nitramine group [66.3 (2)°] rules out further delocalization in the molecule. The geometry of the methylsulfonyl substituent is quasi-tetrahedral, as expected. The crystal packing is stabilized by C—H···O hydrogen bonds, with the molecules arranged in chains extended along the [101] direction.

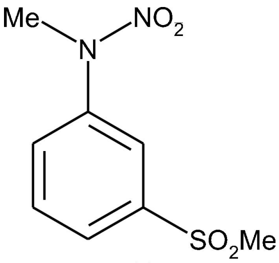
Key indicators

Single-crystal X-ray study
T = 100 K
Mean σ(C–C) = 0.002 Å
R factor = 0.031
wR factor = 0.085
Data-to-parameter ratio = 10.8

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Comment

The properties and molecular structure of compounds containing the *N*-nitroamine group are of interest as they are used in rocket fuels and as explosive substances (Williams, 1982). An interesting feature of *N*-methyl-*N*-phenylnitramine and its derivatives is their ability to undergo a rearrangement at elevated temperature, under acid conditions, and/or on photolysis (Gowenlock *et al.*, 1997), involving the migration of a substituent from the heteroatom to the aromatic ring (Daszkiewicz *et al.*, 2002). Unfortunately, the nature of the rearrangement remains unclear (March, 1985). The molecular structures of secondary arylnitramines may provide a clue to the nature of the rearrangement, and we have recently reported the structures of rearrangement products 5-methylsulfonyl-*N*-methyl-2-nitroaniline and 3-methylsulfonyl-*N*-methyl-2-nitroaniline (Zarychta *et al.*, 2003). These were the main products of the rearrangement of the title compound, 3-methylsulfonyl-*N*-methyl-*N*-nitroaniline, (I), the structure of which we report here (Fig. 1).



(I)

In the molecule, the aromatic ring is slightly deformed. The differences in C—C bond lengths do not exceed 0.02 Å. The ring is almost planar, with dihedral angles around the ring in the range 1.6 (2) to −1.3 (2)°. The parameters that deviate most from the theoretical geometry of the aromatic ring are the valence angles. Angles about the substituted ring C atoms are increased [C6—C1—C2 = 121.68 (14)° and C2—C3—C4 = 121.24 (14)°], with a corresponding decrease in the neighbouring angles. This increase in the endocyclic bond angles at the atoms of the aromatic ring has also been observed in other compounds (Zhukhlistova *et al.*, 2002; Prezhdo *et al.*, 2001). The NNO_2 group is planar; the C3—N1—N2—O3 and C3—N1—N2—O4 torsion angles deviate from the planar geometry by only 0.1 (2) and 0.2 (1)°, respectively. The N1—N2 bond length, 1.3488 (18) Å, is intermediate between that of typical single (1.45 Å) and double (1.25 Å) N—N bonds (Allen *et al.*, 1995), which is a common feature of aromatic nitramines (Daszkiewicz *et al.*, 2002). The C3—N1 bond length, 1.4298 (19) Å, and the torsion angle between the aromatic ring and the nitramine group, 66.30 (19)°, indicates a lack of delocalization in the molecule.

The geometry of the methylsulfonyl group is quasi-tetrahedral, as expected. The S—O and C—S bonds are in good agreement with the corresponding values found for 3-methylsulfonyl-*N*-methyl-2-nitroaniline and 5-methylsulfonyl-*N*-methyl-2-nitroaniline (Zarychta *et al.*, 2003), methyl phenyl sulfone (Chaloner *et al.*, 1992), and *N*,*N*-diethyl-4-(methylsulfonyl)-2-nitro-aniline (MacNicol & Mallinson, 1995). The C1—S1 bond is slightly shorter than that found in 3-methylsulfonyl-*N*-methyl-2-nitroaniline and 5-methylsulfonyl-*N*-methyl-2-nitroaniline [1.7714 (15) Å *versus*. 1.805 (1) and 1.785 (2) Å, respectively; Zarychta *et al.*, 2003]. It is also longer than the corresponding bond in methyl phenyl sulfone (Chaloner *et al.*, 1992) and *N*,*N*-diethyl-4-(methylsulfonyl)-2-nitroaniline (MacNicol & Mallinson, 1995). Such differences in the distortion of the C_{ar}—S bonds suggests that the geometry of the methylsulfonyl group is susceptible to the presence of aromatic ring substituents as well as to crystal packing forces (Chaloner *et al.*, 1992). The C6—C1—S1—O1 torsion angle, 11.20 (15)°, indicates that the methylsulfonyl group is twisted to bring O1 close to the plane of the aromatic ring. This could reinforce a weak O1···H6—C6 hydrogen-bonding interaction.

The crystal packing (Fig. 2) is stabilized by C—H···O hydrogen bonds. The molecules are arranged in chains extended along the [101] direction. Within the chains, groups of four molecules are linked by pairs of C7—H7*A*···O4 and C8—H8*A*···O1 hydrogen bonds.

Experimental

Solid *N*-methyl-3-(methylsulfonyl)aniline (3.7 g, 20 mmol) was added in portions to cold acetic anhydride (30 ml) containing HNO_3 (1.7 ml, 41 mmol, $d = 1.5$). The solution was kept for 2 h at room temperature and was evaporated in a vacuum (323 K). The residue was crystallized and recrystallized from ethanol. 3-Methylsulfonyl-*N*-methyl-*N*-nitroaniline, (I), was obtained (yield 3.3 g, 72%) as colourless crystals melting at 375–376 K. Crystals suitable for X-ray diffraction studies were obtained by slow evaporation of a dichloromethane solution at room temperature. MS, *m*/*z* (int.): 230 (M^+, 2), 184 (100), 105 (66), 104 (27), 77 (11); IR (KBr, cm^{-1}): 1519 (asymmetric stretch of nitro group), 1320, 1293 (envelopes including stretching vibrations of the nitro and sulfonyl groups), 1150 (symmetric stretch of SO_2 group); ^{1}H NMR ($CDCl_3$, p.p.m.): δ 8.01–7.90 (*m*, 2H, aromatic H atoms), 7.72–7.65 (*m*, 2H, aromatic atoms), 3.75 (*s*, 3H, *N*-methyl group), 3.11 (*s*, 3H, *S*-methyl).

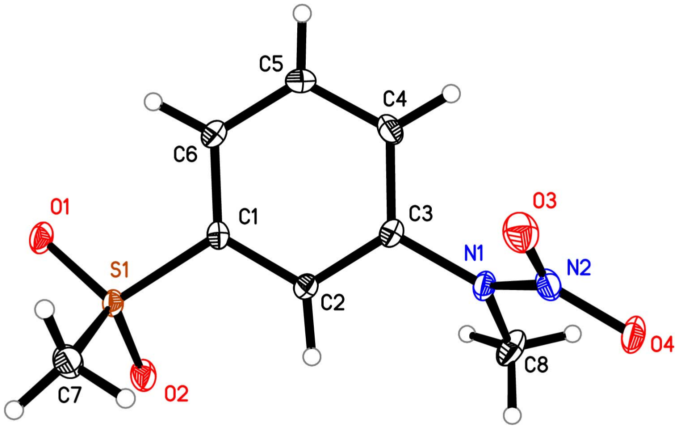


Figure 1
Molecular structure of (I), with atom labels. Displacement ellipsoids are drawn at the 50% probability level.

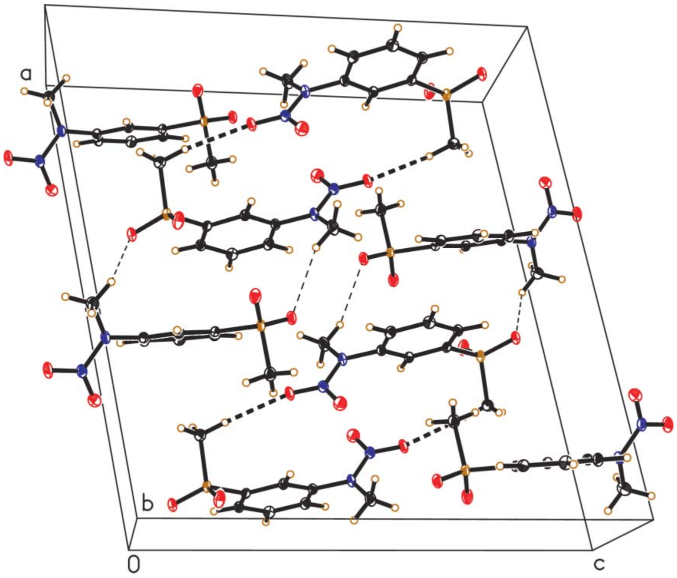


Figure 2
Packing diagram for (I). Hydrogen bonds are drawn as dashed lines.

Crystal data

$C_8H_{10}N_2O_4S$
$M_r = 230.25$
Monoclinic, $C2/c$
$a = 17.489$ (1) Å
$b = 6.816$ (1) Å
$c = 16.528$ (1) Å
$\beta = 100.68$ (1)°
$V = 1936.1$ (3) Å^3
$Z = 8$

$D_x = 1.580$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 5713 reflections
$\theta = 3.1$–26.0°
$\mu = 0.33$ mm^{-1}
$T = 100.0$ (1) K
Irregular fragment, colourless
0.4 × 0.35 × 0.35 mm

Data collection

Oxford Diffraction Xcalibur diffractometer
ω scans
Absorption correction: none
5713 measured reflections
1920 independent reflections

1689 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.025$
$\theta_{\rm max} = 26.0°$
$h = -20 \rightarrow 21$
$k = -7 \rightarrow 8$
$l = -20 \rightarrow 13$

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Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.031$
$wR(F^2) = 0.085$
$S = 1.06$
1907 reflections
176 parameters
All H-atom parameters refined

$w = 1/[\sigma^2(F_o^2) + (0.0513P)^2 + 1.6109P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.48$ e Å^{-3}
$\Delta\rho_{min} = -0.37$ e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
C6—H6···O1	0.95 (2)	2.58 (2)	2.9487 (19)	104 (1)
C7—H7A···O4^{i}	0.96 (2)	2.59 (2)	3.464 (2)	152 (2)
C8—H8A···O1^{ii}	0.95 (2)	2.57 (2)	3.357 (2)	141 (2)

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

13 reflections were rejected and not used in the refinement. All H atoms were refined freely with isotropic displacement parameters.

Data collection: *CrysAlisCCD* (Oxford Diffraction, 2002); cell refinement: *CrysAlisRED* (Oxford Diffraction, 2002); data reduction: *CrysAlisRED*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Sheldrick, 1990); software used to prepare material for publication: *SHELXL97*.

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