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Rearrangement products of 3-methanesulfonyl-*N*-methyl-*N*-nitroaniline

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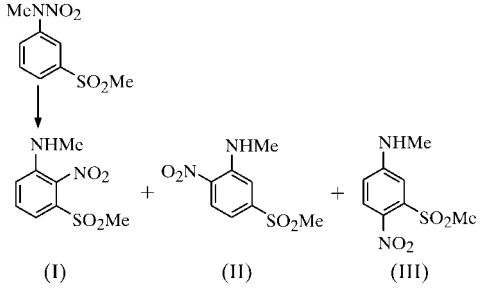
Two isomeric products ($C_8H_{10}N_2O_4S$) of the rearrangement of 3-methanesulfonyl-*N*-methyl-*N*-nitroaniline have been investigated, *viz*. 3-methanesulfonyl-*N*-methyl-2-nitroaniline, which was the main product of the rearrangement, and 5-methanesulfonyl-*N*-methyl-2-nitroaniline. In both molecules, the aromatic rings are appreciably deformed towards *ortho*-quinonoidal geometry by electronic and steric interactions. The crystal structure is stabilized, in both cases, by weak C—H···O hydrogen bonds.

Comment

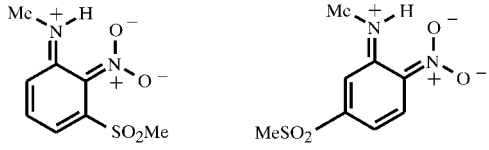
Rearrangement of *N*-(3-chlorophenyl)-*N*-methylnitramine in 0.5 *M* perchloric acid is known to give 3-chloro-*N*-methyl-4-nitroaniline as the main product. *ortho*-Nitro compounds are also formed and, as would be expected, 5-chloro-*N*-methyl-2-nitroaniline prevails over the sterically hindered 3-chloro-*N*-methyl-2-nitroaniline (31 *versus* 18%; White & Klink, 1977). 3-Methanesulfonyl-*N*-methyl-*N*-nitroaniline is much less susceptible to acid-induced rearrangement, but in 40–60% aqueous sulfuric acid it is transformed into the three isomers shown in the *Scheme* below. Surprisingly, (I) is the main



(I) (II) (III)

product of the rearrangement. The ratio of isomers remained nearly constant [(I):(II) = 3.0] in a series of experiments at different temperatures and acid concentrations. Such a result seems to be incompatible with the solvent-caged-pair theory, which used to be considered the correct mechanism of nitramine rearrangement (Williams, 1996).

The molecular structures of the products 3-methanesulfonyl-*N*-methyl-2-nitroaniline, (I), and 5-methanesulfonyl-*N*-methyl-2-nitroaniline, (II), are presented in Figs. 1 and 2. In both molecules, the aromatic rings are strongly deformed by electronic and steric interactions. The differences in C—C bond lengths exceed 0.06 Å in both structures. Such an *ortho*-quinonoid deformation is consistent with the observed geometry of the *N*-methylamino group, which is planar with a relatively short C3—N2 bond (*cf*. Dhaneshwar & Pant, 1972; Viladomat *et al.*, 1998); the valence angles around atom N2 indicate trigonal hybridization of the N atom. The group is almost coplanar with the aromatic ring in (I) [C8—N2—C3—C4 = −2.2 (2)°] and is twisted by only 5.4 (2)° in (II) (Tables 1 and 3), and hence the mesomeric structures presented in the *Scheme* below must contribute to the resonance hybrid.



(I*a*) (II*a*)

The torsion angle along the C4—N1 bond in (II) is −7.6 (2)°, but in the overcrowded molecule of (I), the nitro group is twisted by 35.8 (2)° with respect to the ring plane. This deformation does not completely exclude any interaction with the electron-releasing amino group. We assume that an intramolecular N—H···O hydrogen bond stabilizes the electronic structures represented by (I*a*) and (II*a*). The geometry of the hydrogen bond is very similar in the two molecules, with the atoms of the hydrogen-bonded groups forming an irregular six-membered ring. The donor–acceptor distance is longer in (I) [2.686 (2) *versus* 2.641 (2) Å; Tables 2 and 4], this increase being associated with the large torsion angle (Table 1) along the Ar—NO_2 bond. According to the spectroscopic criteria (Desiraju & Steiner, 1999), these hydrogen bonds are weak; in the FT–IR spectra, recorded in $CDCl_3$ solutions, the

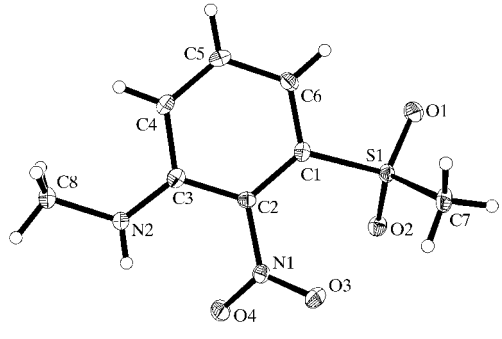


Figure 1
The molecular structure of (I). Displacement ellipsoids are drawn at the 50% probability level.

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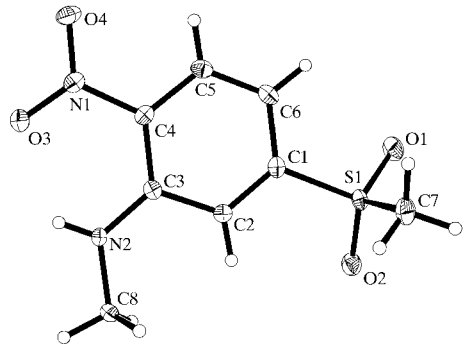

Figure 2
The molecular structure of (II). Displacement ellipsoids are drawn at the 50% probability level.

N—H stretching frequencies are shifted only slightly with respect to the free amine group. In (I), the band appears at 3435 cm^{-1}, and in (II), it appears at 3404 cm^{-1}; for comparison, 3-methanesulfonyl-*N*-methyl-4-nitroaniline absorbs at 3450 cm^{-1} in solution. The methanesulfonyl group seems to be rigid and not susceptible to the deformation caused by steric hindrance. The quasi-tetrahedral geometry of this group is nearly the same in the two molecules. The S—O and S—C bond lengths are slightly larger than in other sulfones (Chaloner *et al.*, 1992; MacNicol & Mallinson, 1995; Shashi Rekha *et al.*, 2000), but this effect may result from intermolecular interactions between strongly polar molecules. The methanesulfonyl groups adopt a conformation such that none of the S—O bonds lies in the ring plane; in (I), the sulfur-bound O atoms are directed away from the nitro group.

Experimental

3-Methanesulfonyl-*N*-methylphenylnitramine was prepared according to the method described by Daszkiewicz *et al.* (1994). The nitramine (0.30 g, 1.3 mmol) was dissolved in dioxane (2 ml) and added to a 50% solution (31.3 g) of sulfuric acid in dioxane and water (6:4). The mixture was maintained at room temperature for 1 h, and then poured on to ice and extracted (4 × 30 ml) with dichloromethane. The extract was dried over anhydrous magnesium sulfate, filtered and evaporated. The mixture of rearrangement products was chromatographed on a column using benzene as eluant. 3-Methanesulfonyl-*N*-methyl-4-nitroaniline was obtained in the pure state. The mixture of *ortho*-isomers (I) and (II) was dissolved in dichloromethane, and the solution was then diluted with diethyl ether and cooled. 5-Methanesulfonyl-*N*-methyl-2-nitroaniline, (II), was collected by filtration and crystallized from toluene, providing orange rod-shaped crystals (m.p. 447.5–448.0 K) suitable for X-ray diffraction. MS *m*/*z* (intensity): 230 (M^+, 73), 213 (6), 182 (6), 149 (21), 124 (24), 105 (100); IR (KBr, cm^{-1}): 3389 (N—H), 1345 (NO_2), 1304, 1140 (SO_2). The mother liquors were re-chromatographed using the preparative layer technique with di-*n*-propyl ether as eluant. 3-Methanesulfonyl-*N*-methyl-2-nitroaniline, (I), was obtained as red prismatic crystals (m.p. 409–411 K). MS *m*/*z* (intensity): 230 (M^+, 100), 213 (37), 201 (5), 185 (13), 147 (6), 121 (24), 105 (100); IR (KBr, cm^{-1}): 3431, 3401 (N—H), 1525, 1354 (NO_2), 1307, 1149 (SO_2).

Compound (I)

Crystal data

$C_8H_{10}N_2O_4S$
M_r = 230.24
Orthorhombic, $P2_12_12_1$
a = 7.631 (3) Å
b = 10.153 (4) Å
c = 12.682 (4) Å
V = 982.6 (6) Å^3
Z = 4
D_x = 1.556 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 7810 reflections
θ = 3.7–29.6°
μ = 0.33 mm^{-1}
T = 96.0 (1) K
Irregular, orange
0.20 × 0.15 × 0.15 mm

Data collection

Xcalibur diffractometer
ω scans
7810 measured reflections
2560 independent reflections
2320 reflections with $I > 2\sigma(I)$
R_{int} = 0.020
θ_{max} = 29.6°
$h = -10 \rightarrow 6$
$k = -14 \rightarrow 13$
$l = -17 \rightarrow 17$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.023
$wR(F^2)$ = 0.056
S = 1.01
2560 reflections
150 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0325P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.29 e Å^{-3}
$\Delta\rho_{min}$ = −0.29 e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.0044 (10)
Absolute structure: Flack (1983), 1040 Friedel pairs
Flack parameter = 0.04 (5)

Table 1
Selected geometric parameters (Å, °) for (I).

S1—O1	1.444 (1)	C1—C6	1.380 (2)
S1—O2	1.450 (1)	C1—C2	1.421 (2)
S1—C7	1.765 (1)	C2—C3	1.424 (2)
S1—C1	1.805 (1)	C3—C4	1.429 (2)
N1—C2	1.449 (2)	C4—C5	1.366 (2)
N2—C3	1.345 (2)		
O1—S1—O2	117.6 (1)	O1—S1—C1	105.9 (1)
O1—S1—C7	106.6 (1)	O2—S1—C1	107.5 (1)
O2—S1—C7	110.4 (1)	C7—S1—C1	108.4 (1)
O1—S1—C1—C6	−11.7 (1)	O3—N1—C2—C3	−141.7 (1)
O2—S1—C1—C6	−138.2 (1)	O4—N1—C2—C3	35.8 (2)
C7—S1—C1—C6	102.4 (1)	C8—N2—C3—C2	175.2 (1)
O1—S1—C1—C2	157.0 (1)	C8—N2—C3—C4	−2.2 (2)
O2—S1—C1—C2	30.5 (1)	C1—C2—C3—N2	176.9 (1)
C7—S1—C1—C2	−88.9 (1)	N1—C2—C3—N2	−6.2 (2)

Table 2
Hydrogen-bonding geometry (Å, °) for (I).

D—H···A	D—H	H···A	D···A	D—H···A
N2—H2···O4	0.84 (2)	2.09 (2)	2.686 (2)	127 (2)
N2—H2···N1	0.84 (2)	2.60 (2)	2.883 (2)	101 (1)
N2—H2···O2^{i}	0.84 (2)	2.31 (2)	3.012 (2)	141 (2)
C6—H6···O1	0.93	2.38	2.7951 (18)	107
C7—H7*B*···O4^{ii}	0.96	2.59	3.3122 (19)	132
C7—H7*B*···O1^{iii}	0.96	2.53	3.2457 (19)	131
C7—H7*C*···O3	0.96	2.33	3.0093 (19)	127

Symmetry codes: (i) $\frac{1}{2}-x, 2-y, z-\frac{1}{2}$; (ii) $\frac{1}{2}-x, 2-y, \frac{1}{2}+z$; (iii) $\frac{1}{2}+x, \frac{3}{2}-y, 1-z$.

Compound (II)

Crystal data

$C_8H_{10}N_2O_4S$
$M_r = 230.25$
Orthorhombic, *Pbca*
$a = 8.567$ (2) Å
$b = 12.330$ (3) Å
$c = 18.343$ (4) Å
$V = 1937.6$ (8) Å^3
$Z = 8$
$D_x = 1.578$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 14 378 reflections
$\theta = 3.7$–$29.8°$
$\mu = 0.33$ mm^{-1}
$T = 96.0$ K
Irregular, orange
0.2 × 0.2 × 0.2 mm

Data collection

Xcalibur diffractometer
ω scans
14 378 measured reflections
2601 independent reflections
2030 reflections with $I > 2\sigma(I)$
$R_{int} = 0.024$
$\theta_{max} = 29.8°$
$h = -11 \rightarrow 11$
$k = -10 \rightarrow 17$
$l = -24 \rightarrow 25$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.031$
$wR(F^2) = 0.114$
$S = 1.16$
2601 reflections
143 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0661P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.42$ e Å^{-3}
$\Delta\rho_{min} = -0.48$ e Å^{-3}

Table 3
Selected geometric parameters (Å, °) for (II).

S1—O1	1.445 (1)	C1—C2	1.374 (2)
S1—O2	1.447 (1)	C1—C6	1.407 (2)
S1—C7	1.762 (2)	C2—C3	1.430 (2)
S1—C1	1.785 (2)	C3—C4	1.431 (2)
N1—C4	1.445 (2)	C4—C5	1.402 (2)
N2—C3	1.347 (2)	C5—C6	1.382 (2)
O1—S1—O2	118.4 (1)	O1—S1—C1	107.7 (1)
O1—S1—C7	108.9 (1)	O2—S1—C1	108.9 (1)
O2—S1—C7	108.6 (1)	C7—S1—C1	103.3 (1)
O1—S1—C1—C2	153.5 (1)	C8—N2—C3—C2	5.4 (2)
O2—S1—C1—C2	23.9 (2)	C8—N2—C3—C4	−174.5 (2)
C7—S1—C1—C2	−91.4 (1)	O4—N1—C4—C5	−7.6 (2)
O1—S1—C1—C6	−27.7 (1)	O3—N1—C4—C5	171.6 (1)
O2—S1—C1—C6	−157.3 (1)	O4—N1—C4—C3	173.6 (1)
C7—S1—C1—C6	87.4 (1)	O3—N1—C4—C3	−7.2 (2)
S1—C1—C2—C3	178.4 (1)	S1—C1—C6—C5	−178.3 (1)

Table 4
Hydrogen-bonding geometry (Å, °) for (II).

D—H···A	D—H	H···A	D···A	D—H···A
N2—H2A···O3	0.84 (2)	2.02 (2)	2.641 (2)	130 (2)
C2—H2···O2	0.93	2.59	2.964 (2)	105
C5—H5···O4	0.93	2.36	2.686 (2)	100
C8—H8B···O4^{iv}	0.96	2.64	3.247 (2)	122
C8—H8C···O1^{v}	0.96	2.50	3.169 (2)	127

Symmetry codes: (iv) $\frac{1}{2} - x, \frac{1}{2} + y, z$; (v) $x, \frac{3}{2} - y, z - \frac{1}{2}$.

Data (to $2\theta = 58°$) were 98.4% complete for (I) and 99.4% complete for (II). In both structures, H atoms of the terminal methyl groups and the aromatic ring were refined using a riding model. The coordinates of H atoms bonded to amine N atoms were refined freely. Compound (I) is a racemate in the bulk sample.

For both compounds, data collection: *CrysAlisCCD* (Oxford Diffraction, 2002); cell refinement: *CrysAlisRED* (Oxford Diffraction, 2002); data reduction: *CrysAlisRED*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *SHELXTL* (Sheldrick, 1990); software used to prepare material for publication: *SHELXL*97.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: JZ1571). Services for accessing these data are described at the back of the journal.

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