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2-[2-Methyl-5-nitro-4-(phenylsulfonylmethyl)imidazol-1-yl]ethanol and 2-methyl-5-nitro-4-phenylsulfonylmethyl-1,3-thiazole

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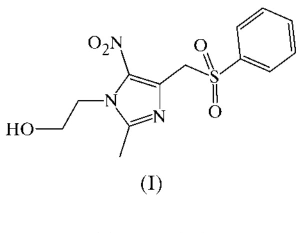
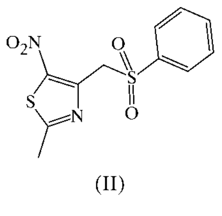
The title compounds, $C_{13}H_{15}N_3O_5S$ and $C_{11}H_{10}N_2O_4S_2$, respectively, both contain a phenylsulfonyl group connected, through a methylene bridge, to either a substituted nitroimidazole or nitro-1,3-thiazole ring. In the imidazole-containing molecule, the nitro and sulfonyl groups are *trans* relative to the sulfonyl–methyl bond, while in the thiazole-containing molecule, these substituents are *cis*. The stabilizing interactions within the crystals are also different between the two compounds.

Comment

5-Nitroimidazoles and 5-nitro-1,3-thiazoles are useful compounds with regard to their biological activities (Nair & Nagarajan, 1983; Kawashima *et al.*, 2001; Andreani *et al.*, 2001). We previously showed that sulfones are relevant synthons in the preparation of new 4-substituted-5-nitroheterocycles (Crozet *et al.*, 2002). In this paper, we describe the X-ray structures of 2-[2-methyl-5-nitro-4-(phenylsulfonylmethyl)imidazol-1-yl]ethanol, (I), and 2-methyl-5-nitro-4-phenylsulfonylmethyl-1,3-thiazole, (II), which are, to our knowledge, the first examples of phenylsulfonylmethyl–nitro heterocyclic compounds to be structurally characterized by single-crystal X-ray diffraction.



(I)



(II)

In both (I) and (II), the nitro group is almost coplanar with the heterocyclic ring; the angles between NO_2 and the mean five-membered-ring plane are 4.2 (3) and 6.7 (1)° for (I) and (II), respectively. The distances and angles involving the various heteroatoms (Tables 1 and 3) are comparable to those observed in other phenylsulfonyl compounds containing a heterocycle (De Bondt *et al.*, 1993; Govindasamy *et al.*, 1998; SethuSankar *et al.*, 2002).

Comparison of the structures of (I) and (II) reveals a difference in the positions of the six- and five-membered rings relative to each other. In (I), the phenyl ring is oriented in the same direction as the nitro group on the imidazole ring, while, in (II), it is oriented in the same direction as the C11 methyl group (Figs. 1 and 2). Looking at this another way, in (I) the nitro and sulfonyl substituents are *trans* relative to one another, while in (II) they are *cis*, with the O atoms pointing in

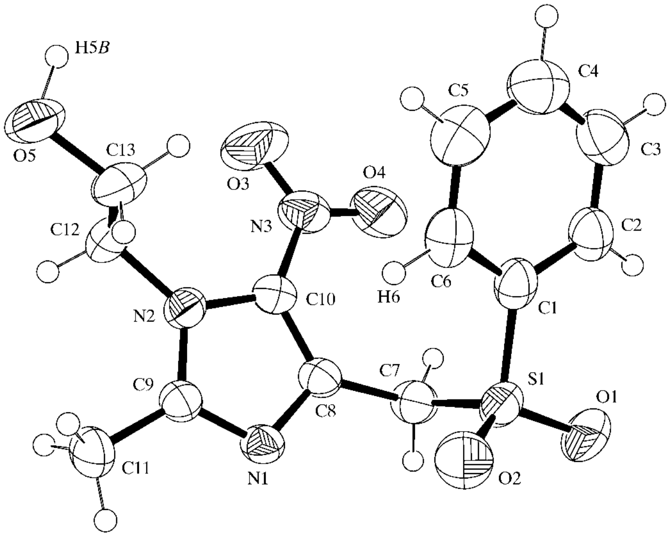


Figure 1
An *ORTEP*II (Johnson, 1976) view of compound (I), showing the atom-labeling scheme and displacement ellipsoids at the 50% probability level.

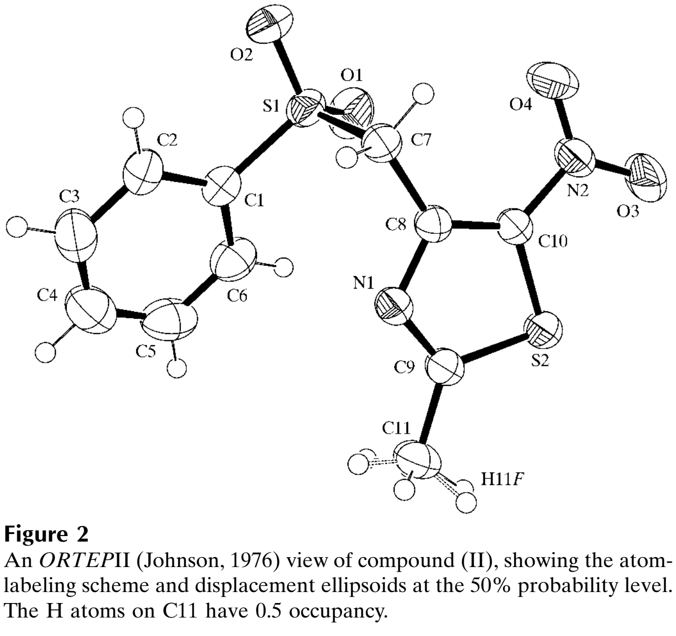


Figure 2
An *ORTEP*II (Johnson, 1976) view of compound (II), showing the atom-labeling scheme and displacement ellipsoids at the 50% probability level. The H atoms on C11 have 0.5 occupancy.

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the same direction; the dihedral angles between the planes defined by NO_2 and SO_2 are 157.1 (2) and 47.6 (2)° in (I) and (II), respectively. To complement this description, for each molecule, we defined the bisector of the NO_2 and SO_2 planes, translated these vectors to a common origin and calculated the angle between them; the values are 134.52 and 40.88° for (I) and (II), respectively, and could be considered as convenient descriptors of the relative orientation of such groups in flexible systems similar to the title compounds. This difference in conformation between the two structures is probably due to the presence of the hydroxyethyl group on the imidazole ring in (I). Indeed, the hydroxyl group is oriented *trans* relative to the heterocycle; the torsion angle N2—C12—C13—O5 is −173.9 (2)°. This involves the hydroxyl group in a hydrogen bond with atom $N1^{i}$ of a molecule of an adjacent cell [symmetry code: (i) $x, y + 1, z$; Table 2]. This hydrogen bond organizes the molecules of (I) in the crystal into an infinite molecular chain parallel to the *b* axis. Finally, the closed conformation adopted by (I) tends to position the two rings in such a way that they can accommodate a weak $C—H\cdots\pi$ interaction; the distance between the centroid of the imidazole ring and atom H6 on C6 is 3.26 Å and the C6—H6···centroid angle is 118°, both of which are in the ranges observed for classical $C—H\cdots\pi$ interactions (Takahashi *et al.*, 1999).

In compound (II), only an intermolecular $C—H\cdots\pi$ interaction can be found, between the thiazole ring and the phenyl ring of a molecule of an adjacent cell; the distance between atom H11*F* on C11 and the centroid of the plane $C1^{ii}/C2^{ii}/C3^{ii}/C4^{ii}/C5^{ii}/C6^{ii}$ is 2.95 Å [symmetry code: (ii) $x + \frac{1}{2}, -y + \frac{3}{2}, z - \frac{1}{2}$], whereas the C11—H11*F*···centroid angle is 165°. A careful look at the packing of the molecules also shows that both compounds are not stabilized in the same way in the crystal. For (I), we can observe two intermolecular π–π stackings involving the aromatic rings; the distance between the centroids of the imidazole ring and the centroid of the phenyl ring of a symmetry-related molecule (symmetry code: $x, -y + \frac{1}{2}, z + \frac{1}{2}$) is 3.481 (1) Å and the dihedral angle between the planes is 6.01°; the distance between the centroid of the phenyl ring and the centroid of the phenyl ring of a molecule in an adjacent cell (symmetry code: $-x, 1 - y, -z$) is 4.872 (1) Å, with a dihedral of 0.03° between the two planes. In compound (II), no such clear interactions can be found; the shortest distances between the various rings of symmetry-related molecules range from 4.336 (1) to 5.253 (1) Å, with dihedral angles ranging from 17.4 to 21.6°.

Experimental

2-[2-Methyl-5-nitro-4-(phenylsulfonylmethyl)imidazol-1-yl]ethanol, (I), was prepared by the vicarious nucleophilic substitution of hydrogen (VNS) method (Makosza & Kwast, 1987) from 2-(2-methyl-5-nitroimidazol-1-yl)ethanol and chloromethyl phenyl sulfone. 2-Methyl-5-nitro-4-phenylsulfonylmethyl-1,3-thiazole, (II), was prepared from 4-chloromethyl-2-methyl-5-nitro-1,3-thiazole and sodium phenylsulfinate *via* an $S_{RN}1$ reaction (Gellis *et al.*, 1997). Suitable crystals of (I) and (II) were grown by slow evaporation from chloroform solutions at room temperature.

Compound (I)

Crystal data

$C_{13}H_{15}N_3O_5S$
$M_r = 325.34$
Monoclinic, $P2_1/c$
$a = 12.5976$ (3) Å
$b = 7.7874$ (3) Å
$c = 14.8929$ (5) Å
$\beta = 94.427$ (2)°
$V = 1456.67$ (8) Å^3
$Z = 4$

$D_x = 1.484$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 2911 reflections
$\theta = 2.4$–26.4°
$\mu = 0.25$ mm^{-1}
$T = 293$ K
Prism, colorless
0.6 × 0.5 × 0.4 mm

Data collection

Nonius KappaCCD diffractometer
φ scans
2911 measured reflections
2726 independent reflections
2509 reflections with $I > 2\sigma(I)$

$R_{\rm int} = 0.045$
$\theta_{\rm max} = 26.4°$
$h = 0 \rightarrow 14$
$k = 0 \rightarrow 9$
$l = -18 \rightarrow 18$

Refinement

Refinement on F^2
$R(F) = 0.046$
$wR(F^2) = 0.113$
$S = 1.07$
2726 reflections
201 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0359P)^2 + 0.6408P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} < 0.001$
$\Delta\rho_{\rm max} = 0.22$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.28$ e Å^{-3}

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

S1—O1	1.4300 (15)	N1—C8	1.3562 (19)
S1—O2	1.4314 (15)	N2—C9	1.353 (2)
S1—C1	1.7537 (19)	N2—C10	1.382 (2)
S1—C7	1.791 (2)	N2—C12	1.472 (2)
O5—C13	1.408 (2)	C8—C10	1.374 (2)
N1—C9	1.328 (2)	C12—C13	1.511 (3)
O1—S1—O2	118.94 (10)	N1—C8—C10	108.71 (13)
C1—S1—C7	105.56 (8)	N1—C9—N2	111.85 (13)
C9—N1—C8	106.62 (13)	C8—C10—N2	107.30 (13)
C9—N2—C10	105.50 (12)	N2—C12—C13	110.99 (14)
C8—C7—S1	112.71 (12)	O5—C13—C12	110.91 (17)

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

D—H···A	D—H	H···A	D···A	D—H···A
O5—H5*B*···N1^{i}	0.82	2.07	2.8562 (19)	162

Symmetry code: (i) $x, 1 + y, z$.

Compound (II)

Crystal data

$C_{11}H_{10}N_2O_4S_2$
$M_r = 298.34$
Monoclinic, $P2_1/n$
$a = 11.1646$ (4) Å
$b = 8.8148$ (2) Å
$c = 13.0731$ (4) Å
$\beta = 93.542$ (2)°
$\gamma = 90.000$ (2)°
$V = 1284.11$ (7) Å^3
$Z = 4$

$D_x = 1.543$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 2911 reflections
$\theta = 2.4$–26.4°
$\mu = 0.43$ mm^{-1}
$T = 293$ K
Prism, colorless
0.5 × 0.4 × 0.4 mm

Data collection

Nonius KappaCCD diffractometer
φ scans
2739 measured reflections
2562 independent reflections
2413 reflections with $I > 2\sigma(I)$

$R_{\rm int} = 0.034$
$\theta_{\rm max} = 26.4°$
$h = 0 \rightarrow 13$
$k = 0 \rightarrow 10$
$l = -16 \rightarrow 16$

Refinement

Refinement on F^2
$R(F) = 0.036$
$wR(F^2) = 0.097$
$S = 1.16$
2562 reflections
172 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0394P)^2 + 0.5975P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} < 0.001$
$\Delta\rho_{\rm max} = 0.22$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.27$ e Å^{-3}

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

S1—O2	1.4384 (14)	S2—C9	1.7184 (18)
S1—O1	1.4383 (15)	N1—C9	1.310 (2)
S1—C1	1.764 (2)	N1—C8	1.363 (2)
S1—C7	1.800 (2)	C8—C10	1.369 (2)
S2—C10	1.7103 (18)		
C1—S1—C7	105.05 (9)	N1—C8—C10	113.11 (15)
C10—S2—C9	88.06 (8)	N1—C9—S2	115.21 (13)
C9—N1—C8	111.60 (15)	C8—C10—S2	112.00 (13)
C8—C7—S1	111.89 (13)		

Most of the H atoms, particularly the H atoms of the hydroxyethyl group of (I), were found in the final difference Fourier map. They were introduced in calculated positions (C—H = 0.93–1.00 Å), but were constrained to their parent atom during the refinement. Disordered H atoms were detected on atom C11 in (II).

For both compounds, data collection: *KappaCCD Reference Manual* (Nonius, 1998); cell refinement: *DENZO* and *SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *DENZO* and *SCALEPACK*; program(s) used to solve structure: *SIR*92 (Altomare *et al.*, 1994); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*II (Johnson, 1976).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: DN1013). Services for accessing these data are described at the back of the journal.

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