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5-Mesylmethoxy-1-(4-nitrophenyl)tetrazole

Alexander S. Lyakhov,[a]* Natalia G. Egorova,[b] Tatiana V. Artamonova,[b] Pavel N. Gaponik[a] and Grigorii I. Koldobskii[b]

[a]Physico-Chemical Research Institute, Belarusian State University, Leningradskaya Street 14, Minsk 220050, Belarus, and [b]St. Petersburg State Institute of Technology, Moskovskii Prospekt 26, St Petersburg 190013, Russian Federation

Correspondence e-mail: lyakhov@bsu.by

Key indicators

Single-crystal X-ray study
T = 292 K
Mean σ(C–C) = 0.003 Å
R factor = 0.039
wR factor = 0.119
Data-to-parameter ratio = 14.2

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

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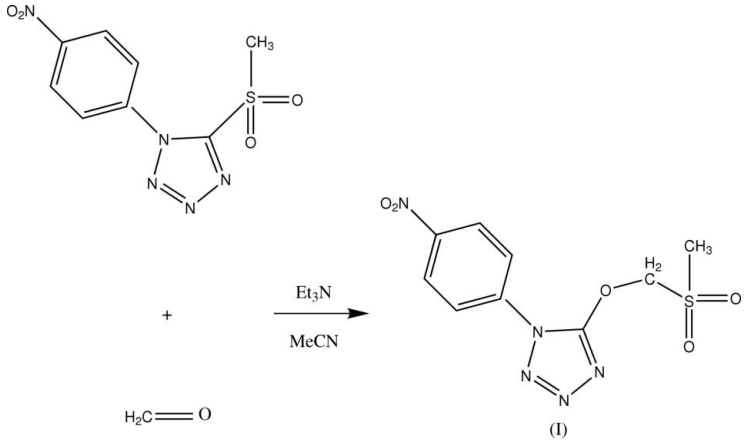
The title compound, $C_9H_9N_5O_5S$, was prepared by the reaction of 5-mesyl-1-(4-nitrophenyl)tetrazole with formaldehyde in a solution of acetonitrile and triethylamine. In the crystal structure, molecules are linked together by a complex set of hydrogen bonds, forming polymeric sheets parallel to the *bc* plane, with van der Waals interactions between them.

Comment

There is significant interest in 1-substituted 5-alkyl- and 5-arylsulfanyltetrazoles, and also other 5-substituted tetrazoles with an S atom in a side-chain, because of their application in the synthesis of highly effective β-lactam antibiotics of the cephalosporin and cephamycin series (Saleh *et al.*, 2003; Powers *et al.*, 2002; Lee *et al.*, 2003). They may also be used for the creation of medicines for the treatment of various forms of tuberculosis (Waisser *et al.*, 1996). In the last decade, great attention has been devoted to the development of preparative methods and to the physico-chemical properties of 5-alkylsulfonyl-1-aryltetrazoles, as well as to the production of new medicines based on them (Koldobskii *et al.*, 2004). To date, only one representative, 2-methoxy-6-[(1-phenyl-5-tetrazolyl)sulfonylmethyl]-1-oxacyclohex-3-ene, has been structurally characterized (Smith *et al.*, 2001). This circumstance is one of the serious obstacles to broadening the application of tetrazoles in pharmaceutical chemistry.



(I)

This work continues our previous investigations of the chemical properties of 1-aryl-5-methylsulfinyl- and 1-aryl-5-mesyltetrazoles (Hrabalek *et al.*, 2004; Egorova *et al.*, 2005). We present here the crystal structure of a new sulfonyltetrazole, *viz*. 5-mesylmethoxy-1-(4-nitrophenyl)tetrazole, (I), prepared by the reaction of 5-mesyl-1-(4-nitrophenyl)tetrazole with formaldehyde in a solution of acetonitrile and

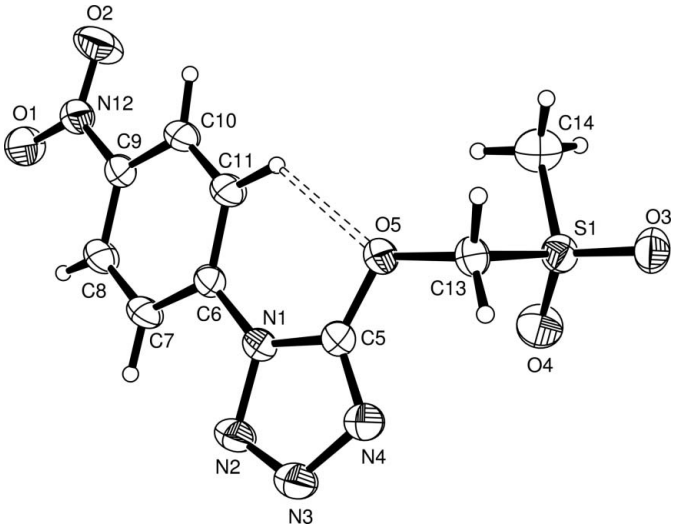


Figure 1
ORTEP-3 plot (Farrugia, 1997) of the molecular structure of (I). Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as spheres of arbitrary radii. The dashed line indicates the intramolecular hydrogen bond.

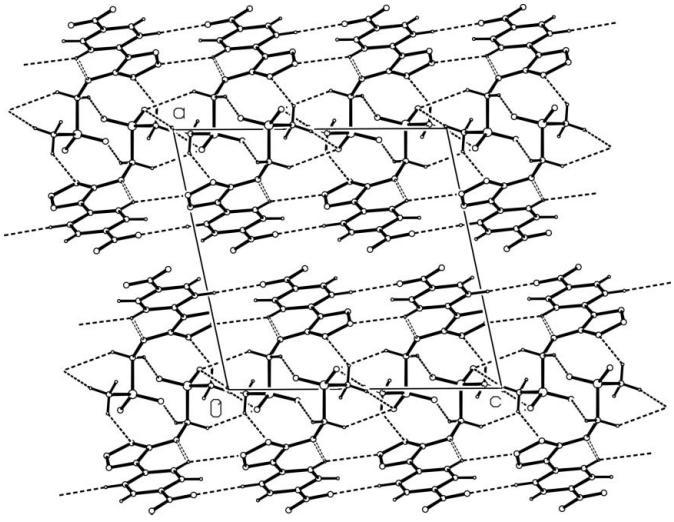


Figure 2
The crystal structure of (I), viwed along the *b* axis. Dashed lines indicate hydrogen bonds.

triethylamine. To date, reactions of this type for tetrazoles have been unknown.

Although the dihedral angle between the least-squares planes of the two rings is rather small [7.98 (10)°], nevertheless the N1—C6 bond length is only slightly shorter than a normal N—C single bond, indicating an absence of conjugation between the two ring systems.

The tetrazole ring geometry is typical of 1,5-disubstituted tetrazoles with alkyl or aryl substituents (Cambridge Structural Database, Version 5.26 of November 2004; Allen, 2002). Formal double bonds N2═N3 and N4═C5 are the shortest of the ring, while the three remaining ring bonds have lengths in a rather narrow range (Table 1). All other geometrical parameters for (I) fall within their expected ranges.

The molecule structure is stabilized by an intramolecular C—H···O hydrogen bond between atom H11 of the benzene ring and O5 of the methoxy group (Table 2). Fig. 2 shows the packing of (I). C—H···O and C—H···N intermolecular hydrogen bonds (Table 2) link the molecules into sheets parallel to the *bc* plane. Any π–π stacking must be extremely weak, because the shortest centroid–centroid separation is 4.915 (2) Å. No C—H···π interactions were identified in a *PLATON* (Spek, 2003) analysis of (I).

Experimental

Triethylamine (1.06 g, 10.5 mmol) and 1 ml of a 37.4% solution of formalin (0.374 g, 12.5 mmol) were added to a solution of 5-mesyl-1-(4-nitrophenyl)tetrazole (2.00 g, 7 mmol) in acetonitrile (25 ml). The reaction mixture was stirred for 1.5 h at 313 K under microwave conditions (25 W). Ethanol (50 ml) was then added to the mixture. The precipitate of (I) was filtered off, dried in air at room temperature and recrystallized from acetonitrile (yield 1.98 g, 89%, m.p. 422–423 K). Analysis found: C 36.12, H 3.01, N 23.51%; calculated for $C_9H_9N_5O_5S$: C 36.12, H 3.01, N 23.41%. ^{1}H NMR (200 MHz, DMSO d_6, δ, p.p.m.): 3.19 (*s*, 3H, CH_3), 5.79 (*s*, 2H, CH_2), 8.03–8.06 (*d*, 2H, Aryl), 8.48–8.50 (*d*, 2H, aryl). IR (KBr, cm^{-1}): ν 943, 975, 1026, 1043, 1097, 1109, 1133, 1151, 1297, 1312, 1323, 1340, 1352, 1368, 1404, 1416, 1445, 1460, 1507, 1522, 1560, 1599, 1619, 2925, 2946, 3019, 3110, 3132, 3450. Single crystals of (I) were prepared by slow evaporation of an ethanol solution at room temperature.

Crystal data

$C_9H_9N_5O_5S$
M_r = 299.27
Monoclinic, $P2_1/c$
a = 12.413 (3) Å
b = 8.093 (3) Å
c = 12.770 (3) Å
β = 101.696 (17)°
V = 1256.2 (6) Å^3
Z = 4
D_x = 1.582 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
θ = 14.8–18.6°
μ = 0.29 mm^{-1}
T = 292 (2) K
Prism, colourless
0.50 × 0.30 × 0.25 mm

Data collection

Nicolet R3m four-circle diffractometer
$\omega/2\theta$ scans
Absorption correction: ψ scan (North *et al.*, 1968)
T_{min} = 0.885, T_{max} = 0.933
3053 measured reflections
2920 independent reflections
2333 reflections with $I > 2\sigma(I)$
R_{int} = 0.014
θ_{max} = 27.6°
$h = 0 \rightarrow 16$
$k = 0 \rightarrow 10$
$l = -16 \rightarrow 16$
3 standard reflections
every 100 reflections
intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.039
$wR(F^2)$ = 0.119
S = 1.07
2920 reflections
206 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.06P)^2 + 0.3301P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.24 e Å^{-3}
$\Delta\rho_{min}$ = −0.32 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

N1—C5	1.342 (2)	N3—N4	1.367 (2)
N1—N2	1.366 (2)	N4—C5	1.301 (2)
N1—C6	1.422 (2)	C5—O5	1.328 (2)
N2—N3	1.282 (3)		
C5—N1—N2	106.30 (15)	C5—N4—N3	104.61 (16)
C5—N1—C6	133.03 (15)	N4—C5—O5	127.63 (17)
N2—N1—C6	120.59 (14)	N4—C5—N1	110.86 (16)
N3—N2—N1	106.70 (15)	O5—C5—N1	121.48 (16)
N2—N3—N4	111.52 (16)		

Table 2
Hydrogen-bond geometry (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C7—H7···O2^{i}	0.96 (3)	2.33 (3)	3.249 (3)	161 (2)
C11—H11···N3^{ii}	0.99 (2)	2.61 (2)	3.444 (3)	141.6 (18)
C13—H13*A*···O4^{iii}	0.96 (2)	2.58 (2)	3.448 (3)	150.9 (17)
C13—H13*B*···O3^{iv}	0.98 (2)	2.49 (2)	3.337 (2)	143.6 (16)
C14—H14*A*···O3^{iv}	0.96	2.58	3.385 (3)	142
C14—H14*C*···N4^{v}	0.96	2.50	3.274 (3)	138
C11—H11···O5	0.99 (2)	2.25 (2)	2.909 (2)	123.0 (18)

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

The H atoms of the methyl group were included in geometrically calculated positions, with C—H = 0.96 Å, and refined using a riding model, with $U_{iso}(H) = 1.5U_{eq}(C)$. The remaining H atoms were found in a difference Fourier map and were refined isotropically.

Data collection: *R3m Software* (Nicolet, 1980); cell refinement: *R3m Software*; data reduction: *R3m Software*; program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997) and *PLATON* (Spek, 2003); software used to prepare material for publication: *SHELXL97* and *PLATON*.

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