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N-Methyl-4-(4-nitrophenyl)-*N*-nitroso-1,3-thiazol-2-amine

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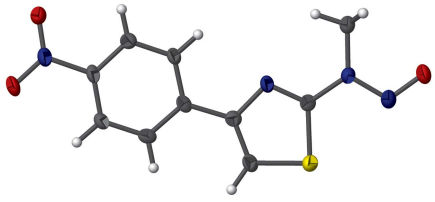
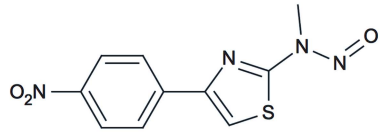
Structural data: full structural data are available from iucrdata.iucr.org

The title compound, $C_{10}H_8N_4O_3S$, is almost planar [dihedral angle between the rings = 2.2 (2)°; r.m.s. deviation for the non-H atoms = 0.050 Å]. In the crystal, C—H···O and C—H···N hydrogen bonds link the molecules into $(10\bar{2})$ layers.

3D view



Chemical scheme



Structure description

The chemistry of *N*-nitrosamines is a subject of considerable interest with regard to their strong carcinogenic and mutagenic properties (Szyrszyng *et al.*, 2001; Loeppky & Outram, 1994; Loeppky *et al.*, 1987). As part of our studies in this area, the synthesis and crystal structure of the title compound are now reported.

There is one independent molecule in the asymmetric unit of the title compound (Fig. 1). The molecule is nearly planar: dihedral angle between the rings = 2.2 (2)°; r.m.s. deviation for the 18 non-hydrogen atoms = 0.050 Å.

The crystal structure features four weak hydrogen bonds (Table 1, Fig. 2), which link the molecules into $(10\bar{2})$ layers. The layers interact only by weak van der Waals interactions.

Synthesis and crystallization

N-methyl-4-(4-nitrophenyl)1,3-thiazol-2-amine (2.0 g, 0.08 mol) was suspended in acetic acid (30 ml). Then, sodium nitrate was added dropwise (0.7 g). After 30 min. the crude yellow precipitate was separated and recrystallized from a solvent mixture of dichloromethane and petrol to yield irregular yellow crystals (0.95 g; melting point = 160–161°C).

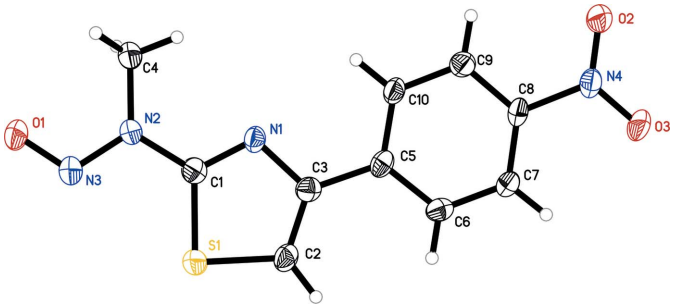


Figure 1
The molecular structure of the title compound, with displacement ellipsoids drawn at the 50% probability level.

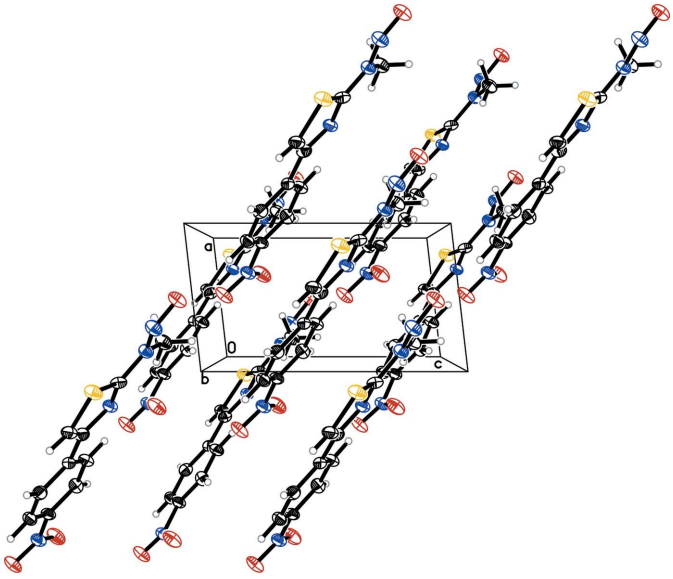


Figure 2
The crystal packing of the title compound, viewed along the *b*-axis direction.

Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2.

References

Loeppky, R. N. & Outram, J. R. (1994). In *N-Nitrosamines and Related N-Nitroso Compounds*. Washington, DC: American Chemical Society.

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

D—H···A	D—H	H···A	D···A	D—H···A
C2—H2···O1^{i}	0.93	2.66	3.182 (6)	117
C2—H2···N3^{i}	0.93	2.48	3.280 (6)	144
C4—H4A···O2^{ii}	0.96	2.60	3.525 (5)	163
C4—H4B···O3^{iii}	0.96	2.52	3.065 (6)	116

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

Table 2
Experimental details.

Crystal data	
Chemical formula	$C_{10}H_8N_4O_3S$
M_r	264.26
Crystal system, space group	Monoclinic, *Pc*
Temperature (K)	85
a, b, c (Å)	4.7729 (3), 13.7362 (8), 8.5391 (4)
β (°)	96.576 (5)
V (Å^3)	556.15 (5)
Z	2
Radiation type	Mo $K\alpha$
μ (mm^{-1})	0.30
Crystal size (mm)	0.28 × 0.17 × 0.15
Data collection	
Diffractometer	Oxford Diffraction Xcalibur
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	2950, 1557, 1320
R_{int}	0.028
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.615
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.038, 0.092, 1.01
No. of reflections	1557
No. of parameters	164
No. of restraints	2
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.29, −0.36

Computer programs: *CrysAlis CCD* (Oxford Diffraction Ltd, 2008), *SHELXS2014* (Sheldrick, 2015*a*), *SHELXL2014* (Sheldrick, 2015*b*) and *SHELXTL* (Sheldrick, 2008).

Loeppky, R. N., Tomasik, W. & Kerrick, B. E. (1987). *Carcinogenesis*, **8**, 941–946.
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Szyrszyng, M., Nowak, E., Gdaniec, M., Milewska, M. J., Herman, A. & Połoński, T. (2001). *J. Org. Chem.* **66**, 7380–7384.

full crystallographic data

IUCrData (2017). **2**, x171121 [https://doi.org/10.1107/S2414314617011211X]

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Crystal data

$C_{10}H_8N_4O_3S$
M_r = 264.26
Monoclinic, *Pc*
a = 4.7729 (3) Å
b = 13.7362 (8) Å
c = 8.5391 (4) Å
β = 96.576 (5)°
V = 556.15 (5) Å^3
Z = 2
F(000) = 272
D_x = 1.578 Mg m^{-3}
Mo *Kα* radiation, *λ* = 0.71073 Å
Cell parameters from 2950 reflections
θ = 3.8–25.9°
μ = 0.30 mm^{-1}
T = 85 K
Irregular, yellow
0.28 × 0.17 × 0.15 mm

Data collection

Oxford Diffraction Xcalibur diffractometer
Radiation source: fine-focus sealed tube
Detector resolution: 1024 x 1024 with blocks 2 x 2 pixels mm^{-1}
ω scan
2950 measured reflections
1557 independent reflections
1320 reflections with $I > 2\sigma(I)$
R_{int} = 0.028
θ_{max} = 25.9°, θ_{min} = 3.8°
h = −5→5
k = −15→16
l = −10→10

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.038
$wR(F^2)$ = 0.092
S = 1.01
1557 reflections
164 parameters
2 restraints
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.061P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.29 e Å^{-3}
$\Delta\rho_{min}$ = −0.36 e Å^{-3}

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Refinement. All H atoms were found in a difference map but set to idealized positions and treated as riding with C_{Ar}—H = 0.93 Å and U_{iso}(H) = 1.2U_{eq}(C) and with C—H_3 = 0.96 Å and U_{iso}(H) = 1.5U_{eq}(C).

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
O1	1.4840 (8)	0.8638 (2)	0.9230 (4)	0.0325 (8)
O2	−0.3222 (7)	0.4737 (2)	0.2371 (4)	0.0354 (9)
O3	−0.4836 (8)	0.5884 (2)	0.0786 (4)	0.0351 (8)
N1	0.7254 (8)	0.7692 (3)	0.5950 (4)	0.0224 (8)
N2	1.1208 (8)	0.8118 (2)	0.7699 (4)	0.0232 (8)
N3	1.2871 (9)	0.8869 (3)	0.8228 (5)	0.0292 (9)
N4	−0.3161 (8)	0.5566 (3)	0.1862 (4)	0.0264 (9)
S1	0.8523 (3)	0.95119 (7)	0.57753 (16)	0.0281 (3)
C1	0.9010 (9)	0.8347 (3)	0.6527 (5)	0.0234 (9)
C2	0.5680 (10)	0.9071 (3)	0.4564 (6)	0.0259 (10)
H2	0.4532	0.9446	0.3845	0.031*
C3	0.5332 (9)	0.8101 (3)	0.4796 (5)	0.0232 (10)
C4	1.1769 (10)	0.7131 (3)	0.8266 (6)	0.0283 (11)
H4A	1.0292	0.6707	0.7816	0.042*
H4B	1.1844	0.7119	0.9394	0.042*
H4C	1.3541	0.6914	0.7962	0.042*
C5	0.3134 (9)	0.7463 (3)	0.3993 (5)	0.0226 (9)
C6	0.1112 (10)	0.7803 (3)	0.2801 (5)	0.0245 (10)
H6	0.1161	0.8449	0.2479	0.029*
C7	−0.0955 (10)	0.7190 (3)	0.2098 (5)	0.0239 (10)
H7	−0.2308	0.7417	0.1313	0.029*
C8	−0.0967 (9)	0.6235 (3)	0.2586 (5)	0.0239 (9)
C9	0.1000 (10)	0.5865 (3)	0.3759 (5)	0.0251 (10)
H9	0.0933	0.5218	0.4071	0.030*
C10	0.3061 (10)	0.6486 (3)	0.4452 (5)	0.0240 (10)
H10	0.4414	0.6252	0.5231	0.029*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.028 (2)	0.0342 (18)	0.0326 (18)	0.0001 (15)	−0.0093 (15)	−0.0021 (13)
O2	0.035 (2)	0.0262 (18)	0.041 (2)	−0.0025 (15)	−0.0119 (17)	−0.0011 (14)
O3	0.031 (2)	0.0381 (18)	0.0320 (18)	−0.0002 (15)	−0.0151 (15)	−0.0006 (14)
N1	0.0174 (19)	0.0251 (17)	0.0237 (19)	0.0004 (15)	−0.0017 (15)	−0.0020 (14)
N2	0.022 (2)	0.0225 (18)	0.0244 (19)	−0.0031 (15)	−0.0008 (16)	−0.0009 (15)
N3	0.028 (2)	0.029 (2)	0.0294 (19)	−0.0030 (18)	−0.0044 (18)	−0.0019 (16)
N4	0.021 (2)	0.030 (2)	0.028 (2)	0.0011 (17)	−0.0035 (16)	−0.0048 (16)
S1	0.0237 (6)	0.0235 (5)	0.0356 (6)	−0.0012 (5)	−0.0033 (4)	0.0000 (5)
C1	0.015 (2)	0.024 (2)	0.031 (2)	0.0013 (18)	0.0042 (18)	−0.0007 (18)
C2	0.017 (3)	0.031 (2)	0.029 (2)	0.0019 (19)	−0.0001 (19)	0.0019 (19)
C3	0.019 (3)	0.024 (2)	0.027 (2)	0.0019 (18)	0.0043 (19)	0.0015 (18)
C4	0.027 (3)	0.026 (2)	0.031 (2)	−0.0021 (19)	−0.004 (2)	−0.0017 (19)
C5	0.016 (2)	0.030 (2)	0.021 (2)	0.0036 (18)	0.0023 (18)	0.0014 (16)
C6	0.024 (2)	0.023 (2)	0.027 (2)	0.0039 (18)	0.0051 (19)	0.0049 (18)
C7	0.021 (2)	0.027 (2)	0.023 (2)	0.0029 (19)	−0.0018 (18)	0.0015 (17)

C8	0.017 (2)	0.030 (2)	0.024 (2)	0.0011 (18)	−0.0027 (18)	−0.0032 (18)
C9	0.028 (3)	0.022 (2)	0.025 (2)	0.002 (2)	0.0001 (19)	−0.0019 (17)
C10	0.019 (3)	0.025 (2)	0.026 (2)	0.0030 (18)	−0.0040 (18)	−0.0016 (17)

Geometric parameters (Å, º)

O1—N3	1.238 (5)	C4—H4A	0.9600
O2—N4	1.220 (4)	C4—H4B	0.9600
O3—N4	1.227 (5)	C4—H4C	0.9600
N1—C1	1.288 (6)	C5—C10	1.399 (6)
N1—C3	1.386 (6)	C5—C6	1.400 (6)
N2—N3	1.348 (5)	C6—C7	1.381 (6)
N2—C1	1.401 (5)	C6—H6	0.9300
N2—C4	1.454 (5)	C7—C8	1.376 (6)
N4—C8	1.475 (5)	C7—H7	0.9300
S1—C2	1.720 (5)	C8—C9	1.388 (6)
S1—C1	1.730 (4)	C9—C10	1.383 (6)
C2—C3	1.359 (6)	C9—H9	0.9300
C2—H2	0.9300	C10—H10	0.9300
C3—C5	1.475 (6)		
C1—N1—C3	109.7 (3)	N2—C4—H4C	109.5
N3—N2—C1	115.6 (3)	H4A—C4—H4C	109.5
N3—N2—C4	121.6 (4)	H4B—C4—H4C	109.5
C1—N2—C4	122.8 (3)	C10—C5—C6	119.1 (4)
O1—N3—N2	114.0 (3)	C10—C5—C3	118.6 (4)
O2—N4—O3	124.0 (4)	C6—C5—C3	122.3 (4)
O2—N4—C8	118.5 (4)	C7—C6—C5	120.7 (4)
O3—N4—C8	117.5 (4)	C7—C6—H6	119.6
C2—S1—C1	87.7 (2)	C5—C6—H6	119.6
N1—C1—N2	121.2 (4)	C8—C7—C6	118.5 (4)
N1—C1—S1	116.8 (4)	C8—C7—H7	120.7
N2—C1—S1	122.0 (3)	C6—C7—H7	120.7
C3—C2—S1	111.0 (4)	C7—C8—C9	122.7 (4)
C3—C2—H2	124.5	C7—C8—N4	119.6 (4)
S1—C2—H2	124.5	C9—C8—N4	117.6 (4)
C2—C3—N1	114.8 (4)	C10—C9—C8	118.2 (4)
C2—C3—C5	127.4 (4)	C10—C9—H9	120.9
N1—C3—C5	117.8 (3)	C8—C9—H9	120.9
N2—C4—H4A	109.5	C9—C10—C5	120.7 (4)
N2—C4—H4B	109.5	C9—C10—H10	119.6
H4A—C4—H4B	109.5	C5—C10—H10	119.6
C1—N2—N3—O1	−178.1 (4)	C2—C3—C5—C6	2.2 (6)
C4—N2—N3—O1	−0.9 (6)	N1—C3—C5—C6	−179.4 (4)
C3—N1—C1—N2	−178.9 (3)	C10—C5—C6—C7	0.9 (6)
C3—N1—C1—S1	0.8 (5)	C3—C5—C6—C7	−178.5 (4)
N3—N2—C1—N1	−178.8 (4)	C5—C6—C7—C8	−0.5 (6)

C4—N2—C1—N1	4.1 (6)	C6—C7—C8—C9	0.4 (6)
N3—N2—C1—S1	1.6 (5)	C6—C7—C8—N4	179.6 (4)
C4—N2—C1—S1	−175.6 (4)	O2—N4—C8—C7	−176.1 (4)
C2—S1—C1—N1	−0.1 (4)	O3—N4—C8—C7	3.3 (6)
C2—S1—C1—N2	179.5 (4)	O2—N4—C8—C9	3.2 (6)
C1—S1—C2—C3	−0.6 (4)	O3—N4—C8—C9	−177.4 (4)
S1—C2—C3—N1	1.2 (5)	C7—C8—C9—C10	−0.5 (6)
S1—C2—C3—C5	179.7 (3)	N4—C8—C9—C10	−179.8 (4)
C1—N1—C3—C2	−1.3 (5)	C8—C9—C10—C5	0.8 (6)
C1—N1—C3—C5	−179.9 (4)	C6—C5—C10—C9	−1.0 (6)
C2—C3—C5—C10	−177.2 (4)	C3—C5—C10—C9	178.4 (4)
N1—C3—C5—C10	1.2 (5)		

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C2—H2···O1^{i}	0.93	2.66	3.182 (6)	117
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