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Crystal structure of *C*-2-benzothiazole-*N*-methylnitrone

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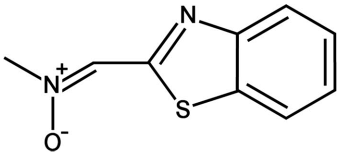
The molecule of the title compound {systematic name: *N*-[(benzothiazol-2-yl)methylidene]methylamine *N*-oxide}, $C_9H_8N_2OS$, is close to planar [maximum deviation from the mean plane = 0.081 (2) Å], its conformation being stabilized by a strong intramolecular attractive S···O interaction [2.6977 (16) Å]. In the crystal, molecules are linked into centrosymmetric dimers by pairs of weak C—H···O hydrogen bonds.

Keywords: crystal structure; benzothiazole; nitrone; S···O attractive interaction.

CCDC reference: 1411951

1. Related literature

For the 1,3-dipolar cycloaddition reaction of nitrones, see: Tufariello (1984); Torssell (1988). For the properties of benzothiazole derivatives, see: Bradshaw *et al.* (2002); Paramashivappa *et al.* (2003); Jimonet *et al.* (1999); Ul-Hasan *et al.* (2002); Şener *et al.* (2000); Mruthyunjayaswamy & Shanthaveerappa (2000); Arpaci *et al.* (2002). For work by our group on nitrones, see: Doroschuk *et al.* (2006); Raspertova *et al.* (2002); Petkova *et al.* (2001). For attractive S—O interactions, see: Mokhir *et al.* (1999). For N—O bond lengths in nitrones, see: Ruano *et al.* (2012). For van der Waals radii, see: Wells (1986). For the synthesis, see: Delpierre & Lamchen (1965).



2. Experimental

2.1. Crystal data

$C_9H_8N_2OS$
$M_r = 192.23$
Triclinic, $P\bar{1}$
$a = 5.5253$ (14) Å
$b = 7.4528$ (19) Å
$c = 10.839$ (4) Å
$\alpha = 83.51$ (2)°
$\beta = 85.79$ (3)°
$\gamma = 77.39$ (3)°
$V = 432.2$ (2) Å^3
$Z = 2$
Mo $K\alpha$ radiation
$\mu = 0.33$ mm^{-1}
$T = 294$ K
0.4 × 0.3 × 0.2 mm

2.2. Data collection

Oxford Diffraction Xcalibur 3 diffractometer
Absorption correction: multi-scan (*CrysAlis PRO*; Agilent, 2011)
$T_{\min} = 0.423$, $T_{\max} = 0.994$
3491 measured reflections
1933 independent reflections
1477 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.018$

2.3. Refinement

$R[F^2 > 2\sigma(F^2)] = 0.033$
$wR(F^2) = 0.087$
$S = 1.00$
1933 reflections
130 parameters
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{\max} = 0.24$ e Å^{-3}
$\Delta\rho_{\min} = -0.19$ e Å^{-3}

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C5—H5···O1$^{\rm i}$	0.93	2.53	3.331 (2)	145

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

Data collection: *CrysAlis PRO* (Agilent, 2011); cell refinement: *CrysAlis PRO*; data reduction: *CrysAlis PRO*; program(s) used to solve structure: *SHELXT* (Sheldrick, 2015*a*); program(s) used to refine structure: *SHELXL2014* (Sheldrick, 2015*b*); molecular graphics: *OLEX2* (Dolomanov *et al.*, 2009); software used to prepare material for publication: *OLEX2*.

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Supporting information for this paper is available from the IUCr electronic archives (Reference: RZ5162).

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Crystal structure of *C*-2-benzothiazole-*N*-methylnitrone

Roman Doroschuk

S1. Chemical context

One of the most important approaches for the symthesis of various five-membered heterocyclic systems is the 1,3-dipolar cycloaddition reaction. The use as dipoles of compounds such as nitrile oxides and nitrones leads to a wide range of N,O-containing heterocyclic systems (isoxazole, isoxazoline, isoxazolidine; Tufariello, 1984), which have biological activity and can be used as starting materials for the synthesis of acyclic compounds (for example, 1,3-aminoalcohols by cleavage of the N–O bond; Torssell, 1988). On the other hand, compounds containing the benzothiazole moiety are of biological and industrial interest. In fact, benzothiazole derivatives possess a wide spectrum of biological applications such as anti-tumor (Bradshaw *et al.*, 2002), anti-inflammatory (Paramashivappa *et al.*, 2003), anticonvulsant (Jimonet *et al.*, 1999), and antimicrobial activities (Ul-Hasan *et al.*, 2002; Şener *et al.*, 2000; Mruthyunjayaswamy *et al.*, 2000; Arpaci *et al.*, 2002).

Following our studies on aromatic nitrone (Doroschuk *et al.*, 2006; Raspertova *et al.*, 2002; Petkova *et al.*, 2001) in this paper we describe the structure of *C*-2-benzothiazole-*N*-methylnitrone.

S2. Structural commentary

In the molecule of the title compound (Fig. 1), the oxygen atom of the nitrone group exists in *syn*-conformation with respect to the sulfur atom of the benzothiazole moiety. This conformation is achieved due to a strong electrostatic intra-molecular attractive S···O interaction. Thus, the S1···O1 distance (2.6977 (16) Å) is significantly shorter than the sum of the van der Waals radii of O and S (1.5 and 1.85 Å, respectively; Wells, 1986). A similar attractive S···O interaction is characteristic for molecules containing the thiazole moiety (Mokhir *et al.*, 2002). The value of the N1—C2 bond length (1.298 (2) Å) is typical for a C═N bond (1.28 Å; Wells, 1986), while the N1—O1 bond length (1.2763 (17) Å) is slightly shorter than those usually observed for nitrone N—O bonds (Petkova *et al.*, 2001; Ruano *et al.*, 2012). The heterocyclic ring system and the nitrone fragment C1—N1—O1—C2 are almost coplanar (the maximum deviation from the least-squares mean plane is 0.081 (2) Å for atom C1), forming a dihedral angle of 3.40 (9)°. The bond lengths within the benzothiazole ring system are unexceptional.

S3. Supramolecular features

In the crystal (Fig. 2), centrosymmetrically-related molecules are linked into dimers *via* pairs of C—H···O hydrogen bonds (Table 1).

S4. Synthesis and crystallization

C-2-Benzothiazole-*N*-methylnitrone was synthesized by condensation of the corresponding aldehyde with N-methyl-hydroxylamine hydrochloride in the presence of base (Delpierre & Lamchen, 1965).

2-Benzothiazolecarbaldehyde (0.1632 g, 0.01 mol), CH_2CL_2 (20 ml), and *N*-metylhydroxylamine hydrochloride (0.9175 g, 0.011 mol) were placed in a 50 mL flask, and the mixture was stirred at room temperature. To the resulting solution was added $NaHCO_3$ (2.7675 g, 0.033 mol). The reaction mixture was reluxed for 3 h. The NaCl precipitate and excess of sodium bicarbonate was removed by filtration, and the filtrate was evaporated to give a solid (1.83g, yield 95%). The solid was recrystallized from an absolute hexane solution.

S5. Refinement

One aromatic H atom (H6) could be located in a difference Fourier map and was refined freely. All other H atoms were placed geometrically and treated as riding, with C—H = 0.93-0.96 Å, and $U_{\rm iso}$(H) = $1.5U_{\rm eq}$(C) for methyl H atoms or $1.2U_{\rm eq}$(C) otherwise. A rotating model was used for the methyl H atoms. 36 outliers were omitted in the last cycles of refinement.

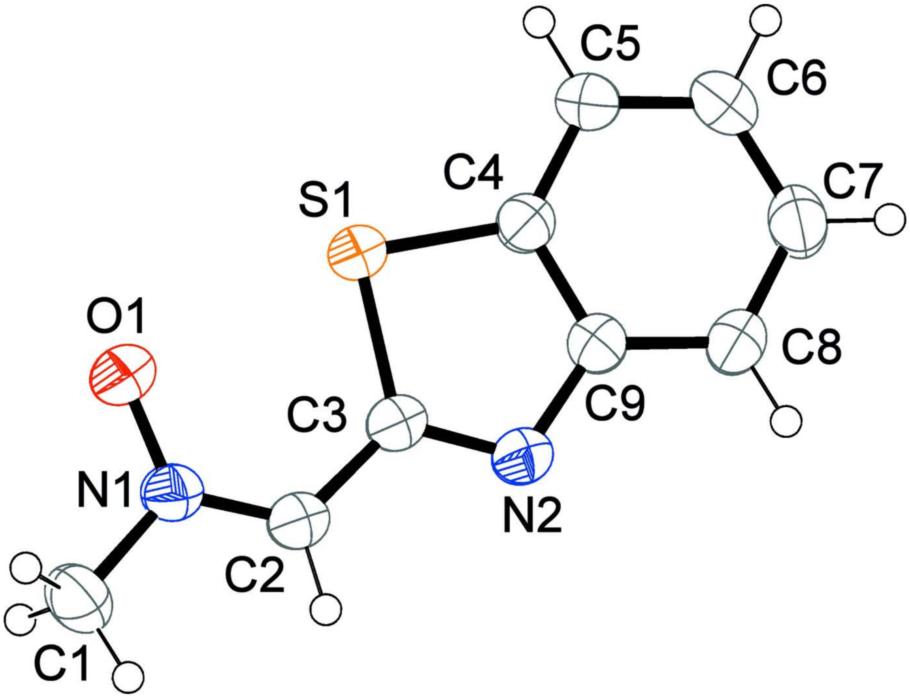

Figure 1

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

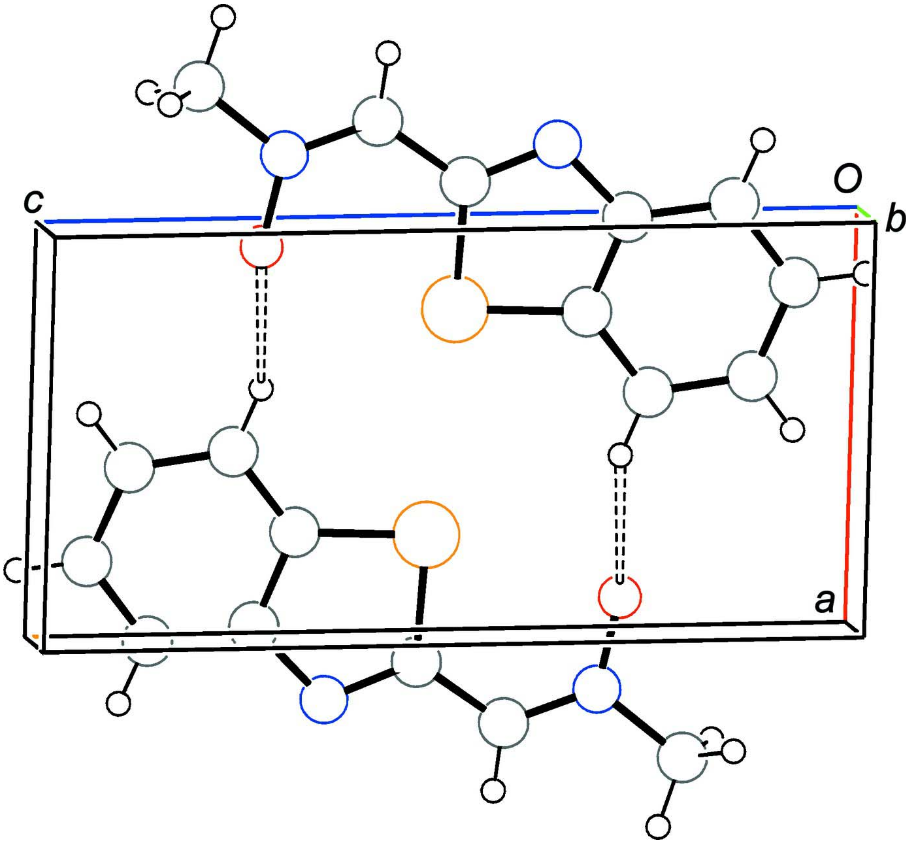

Figure 2

Partial crystal packing of the title compound approximately viewed along [0 1 0], showing the formation of a dimeric unit through a pair of C—H···O hydrogen bonds (dashed lines).

N-[(Benzothiazol-2-yl)methylidene]methylamine *N*-oxide

Crystal data

$C_9H_8N_2OS$
$M_r = 192.23$
Triclinic, $P\overline{1}$
$a = 5.5253$ (14) Å
$b = 7.4528$ (19) Å
$c = 10.839$ (4) Å
$\alpha = 83.51$ (2)°
$\beta = 85.79$ (3)°
$\gamma = 77.39$ (3)°
$V = 432.2$ (2) Å^3

$Z = 2$
$F(000) = 200$
$D_x = 1.477$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 110 reflections
$\theta = 18.2$–8.2°
$\mu = 0.33$ mm^{-1}
$T = 294$ K
Block, colourless
0.4 × 0.3 × 0.2 mm

Data collection

Oxford Diffraction Xcalibur 3 diffractometer
Detector resolution: 16.1827 pixels mm^{-1}
ω scans
Absorption correction: multi-scan (*CrysAlis PRO*; Agilent, 2011)
$T_{\min} = 0.423$, $T_{\max} = 0.994$
3491 measured reflections

1933 independent reflections
1477 reflections with $I > 2\sigma(I)$
$R_{\text{int}} = 0.018$
$\theta_{\max} = 27.5°$, $\theta_{\min} = 2.8°$
$h = -7 \rightarrow 7$
$k = -9 \rightarrow 9$
$l = -14 \rightarrow 14$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.033$
$wR(F^2) = 0.087$
$S = 1.00$
1933 reflections
130 parameters
0 restraints
Primary atom site location: structure-invariant direct methods

Hydrogen site location: inferred from neighbouring sites
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0521P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.24$ e Å^{-3}
$\Delta\rho_{min} = -0.19$ e Å^{-3}

Special details

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

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	y	z	U_{iso}*/U_{eq}
O1	0.0619 (2)	0.21490 (18)	0.72954 (11)	0.0573 (3)
S1	0.22145 (7)	0.17869 (5)	0.49058 (4)	0.04032 (14)
N1	−0.1621 (2)	0.29247 (17)	0.70659 (12)	0.0406 (3)
N2	−0.1774 (2)	0.33921 (18)	0.37522 (12)	0.0415 (3)
C1	−0.3325 (3)	0.3346 (3)	0.81411 (16)	0.0536 (4)
H1A	−0.2936	0.4351	0.8513	0.091 (8)*
H1B	−0.3159	0.2277	0.8738	0.078 (7)*
H1C	−0.5000	0.3688	0.7878	0.100 (8)*
C2	−0.2414 (3)	0.3343 (2)	0.59501 (14)	0.0402 (3)
H2	−0.4066	0.3938	0.5861	0.048 (5)*
C3	−0.0891 (3)	0.2941 (2)	0.48533 (14)	0.0366 (3)
C4	0.2333 (3)	0.1897 (2)	0.33030 (14)	0.0368 (3)
C5	0.4328 (3)	0.1236 (2)	0.25071 (15)	0.0423 (4)
H5	0.5858	0.0644	0.2813	0.049 (5)*
C6	0.3978 (3)	0.1484 (2)	0.12546 (16)	0.0470 (4)
H6	0.531 (3)	0.098 (2)	0.0729 (18)	0.058 (5)*
C7	0.1702 (3)	0.2371 (2)	0.07882 (15)	0.0503 (4)
H7	0.1516	0.2513	−0.0065	0.055 (5)*
C8	−0.0273 (3)	0.3040 (2)	0.15698 (15)	0.0483 (4)
H8	−0.1790	0.3640	0.1253	0.065 (6)*
C9	0.0036 (3)	0.2802 (2)	0.28572 (14)	0.0385 (3)

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0454 (7)	0.0711 (8)	0.0454 (7)	0.0102 (6)	−0.0084 (5)	−0.0037 (6)
S1	0.0344 (2)	0.0451 (2)	0.0377 (2)	0.00088 (15)	−0.00453 (15)	−0.00450 (15)
N1	0.0385 (7)	0.0394 (7)	0.0402 (7)	−0.0011 (5)	−0.0012 (5)	−0.0029 (5)
N2	0.0322 (7)	0.0500 (7)	0.0399 (7)	−0.0034 (6)	−0.0031 (5)	−0.0038 (6)

C1	0.0562 (11)	0.0594 (11)	0.0411 (9)	−0.0060 (8)	0.0077 (8)	−0.0069 (8)
C2	0.0344 (8)	0.0425 (8)	0.0415 (8)	−0.0033 (6)	−0.0033 (6)	−0.0032 (7)
C3	0.0331 (7)	0.0355 (8)	0.0404 (8)	−0.0051 (6)	−0.0043 (6)	−0.0030 (6)
C4	0.0367 (8)	0.0362 (7)	0.0375 (8)	−0.0072 (6)	−0.0035 (6)	−0.0035 (6)
C5	0.0374 (8)	0.0431 (8)	0.0443 (8)	−0.0024 (6)	−0.0012 (7)	−0.0082 (7)
C6	0.0472 (9)	0.0492 (9)	0.0443 (9)	−0.0083 (7)	0.0086 (7)	−0.0133 (7)
C7	0.0555 (10)	0.0605 (10)	0.0359 (8)	−0.0128 (8)	−0.0020 (7)	−0.0081 (8)
C8	0.0420 (9)	0.0608 (10)	0.0402 (9)	−0.0055 (7)	−0.0086 (7)	−0.0030 (8)
C9	0.0369 (8)	0.0410 (8)	0.0376 (8)	−0.0076 (6)	−0.0024 (6)	−0.0049 (6)

Geometric parameters (Å, º)

O1—N1	1.2763 (17)	C2—C3	1.426 (2)
S1—C3	1.7456 (16)	C4—C5	1.386 (2)
S1—C4	1.7269 (17)	C4—C9	1.393 (2)
N1—C1	1.461 (2)	C5—H5	0.9300
N1—C2	1.298 (2)	C5—C6	1.371 (2)
N2—C3	1.303 (2)	C6—H6	0.934 (19)
N2—C9	1.377 (2)	C6—C7	1.389 (3)
C1—H1A	0.9600	C7—H7	0.9300
C1—H1B	0.9600	C7—C8	1.371 (2)
C1—H1C	0.9600	C8—H8	0.9300
C2—H2	0.9300	C8—C9	1.405 (2)
C4—S1—C3	88.33 (8)	C5—C4—C9	121.64 (14)
O1—N1—C1	116.50 (13)	C9—C4—S1	109.96 (12)
O1—N1—C2	123.49 (13)	C4—C5—H5	121.0
C2—N1—C1	120.01 (13)	C6—C5—C4	117.98 (15)
C3—N2—C9	109.93 (12)	C6—C5—H5	121.0
N1—C1—H1A	109.5	C5—C6—H6	117.3 (12)
N1—C1—H1B	109.5	C5—C6—C7	121.45 (15)
N1—C1—H1C	109.5	C7—C6—H6	121.2 (12)
H1A—C1—H1B	109.5	C6—C7—H7	119.6
H1A—C1—H1C	109.5	C8—C7—C6	120.85 (15)
H1B—C1—H1C	109.5	C8—C7—H7	119.6
N1—C2—H2	118.2	C7—C8—H8	120.6
N1—C2—C3	123.58 (14)	C7—C8—C9	118.84 (16)
C3—C2—H2	118.2	C9—C8—H8	120.6
N2—C3—S1	116.37 (11)	N2—C9—C4	115.40 (14)
N2—C3—C2	121.29 (13)	N2—C9—C8	125.36 (14)
C2—C3—S1	122.33 (11)	C4—C9—C8	119.24 (15)
C5—C4—S1	128.40 (12)		
O1—N1—C2—C3	1.7 (2)	C4—S1—C3—C2	178.11 (13)
S1—C4—C5—C6	179.91 (13)	C4—C5—C6—C7	0.1 (3)
S1—C4—C9—N2	−0.08 (17)	C5—C4—C9—N2	−179.70 (14)
S1—C4—C9—C8	−179.91 (12)	C5—C4—C9—C8	0.5 (2)
N1—C2—C3—S1	1.4 (2)	C5—C6—C7—C8	0.4 (3)

N1—C2—C3—N2	−179.90 (14)	C6—C7—C8—C9	−0.4 (3)
C1—N1—C2—C3	−178.46 (14)	C7—C8—C9—N2	−179.78 (15)
C3—S1—C4—C5	179.96 (15)	C7—C8—C9—C4	0.0 (2)
C3—S1—C4—C9	0.38 (11)	C9—N2—C3—S1	0.71 (17)
C3—N2—C9—C4	−0.39 (19)	C9—N2—C3—C2	−178.07 (13)
C3—N2—C9—C8	179.43 (15)	C9—C4—C5—C6	−0.5 (2)
C4—S1—C3—N2	−0.65 (12)		

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C5—H5···O1^{i}	0.93	2.53	3.331 (2)	145

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