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2-Morpholino-4-oxo-4,5-dihydrothiophene-3-carbonitrile

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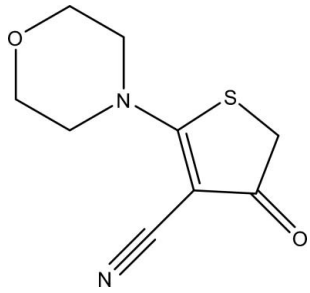
Key indicators: single-crystal X-ray study; T = 100 K; mean σ(C–C) = 0.002 Å; R factor = 0.026; wR factor = 0.068; data-to-parameter ratio = 12.6.

The title compound, $C_9H_{10}N_2O_2S$, was obtained from the treatment of ethyl 4-cyano-3-hydroxy-5-morpholinothiophene-2-carboxylate with concentrated HCl. The mean plane of the essentially planar dihydrothiophene ring is almost orthogonal to the mirror plane of the *N*-morpholine substituent, making a dihedral angle of 87.2 (2)°.

Related literature

For the structure of a similar compound with the morpholine substituent attached to dihydrothiophene ring, see: Moghaddam *et al.* (2005).



Experimental

Crystal data

$C_9H_{10}N_2O_2S$
M_r = 210.25
Monoclinic, $P2_1/c$
a = 7.1931 (3) Å
b = 17.3275 (8) Å
c = 7.2793 (3) Å
β = 94.506 (2)°
V = 904.48 (7) Å^3
Z = 4
Cu $K\alpha$ radiation
μ = 2.98 mm^{-1}
T = 100 K
0.41 × 0.20 × 0.08 mm

Data collection

Bruker Kappa APEXII diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2001)
T_{min} = 0.765, T_{max} = 0.919
7337 measured reflections
1607 independent reflections
1531 reflections with $I > 2\sigma(I)$
R_{int} = 0.027

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.026
$wR(F^2)$ = 0.068
S = 1.08
1607 reflections
128 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.29 e Å^{-3}
$\Delta\rho_{min}$ = −0.20 e Å^{-3}

Data collection: *APEX2* (Bruker, 2007); cell refinement: *SAINT* (Bruker, 2007); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL*.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: DN2498).

References

Bruker (2001). *SADABS*. Bruker AXS Inc., Madison, Wisconsin, USA.
Bruker (2007). *APEX2* and *SAINT*. Bruker AXS Inc., Madison, Wisconsin, USA.
Moghaddam, F. M., Boeini, H. Z., Bagheri, M., Ruëdi, P. & Linden, A. (2005). *Sulfur Chem.* **26**, 245–250.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.

supporting information

Acta Cryst. (2009). E**65**, o2765 [https://doi.org/10.1107/S1600536809041737]

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S1. Comment

The title compound was obtained *via* the treatment of ethyl 4-cyano-3-hydroxy-5-morpholinothiophene-2-carboxylate with concentrated HCl, and its structural formula was confirmed by the present study (Fig. 1).

Dihydrothiophene ring C5/C6/C7/C8/S1 is planar within 0.02 Å. Its least squares plane is almost orthogonal to the mirror plane of the *N*-morpholine substituent passing through C5, N1 and O1 atoms: the corresponding dihedral angle being 92.8 (2)°. Similar conformation is observed in the related structure with morpholine substituent attached to dihydrothiophene ring (Moghaddam *et al.*, 2005).

S2. Experimental

Into a suspension of ethyl 4-cyano-3-hydroxy-5-morpholinothiophene-2-carboxylate (100 mg, 0.35 mmol) in MeOH (1.2 ml), was added concentrated HCl (0.2 ml) with stirring. The reaction mixture was heated in an oil bath at 60°C for 48 h to form a clear solution. The reaction solution was cooled to room temperature and the solvent was removed under reduced pressure. The resulting residue was neutralized with 2 N NaOH to pH 4. The precipitate was collected by filtration and rinsed with a solution of water/MeOH. The sample was dried under high vacuum to afford the desired compound as a white solid (52.1 mg, 58% yield). LC—MS (APCI, *M*+1) 211.2; ^{1}H NMR (300 MHz, DMSO-d$_6$) δ p.p.m. 3.87 (s, 3 H), 3.84 (dd, J=5.84, 2.07 Hz, 2 H), 3.68 - 3.79 (m, 5 H). The product was recrystallized from EtOAc/hexane/dichloromethane to yield single crystals suitable for X-ray diffraction studies.

S3. Refinement

All H atoms were placed in geometrically calculated positions (C—H 0.99 Å) and included in the refinement in riding motion approximation. The U_{iso}(H) were set to 1.2U_{eq} of the carrying atom.

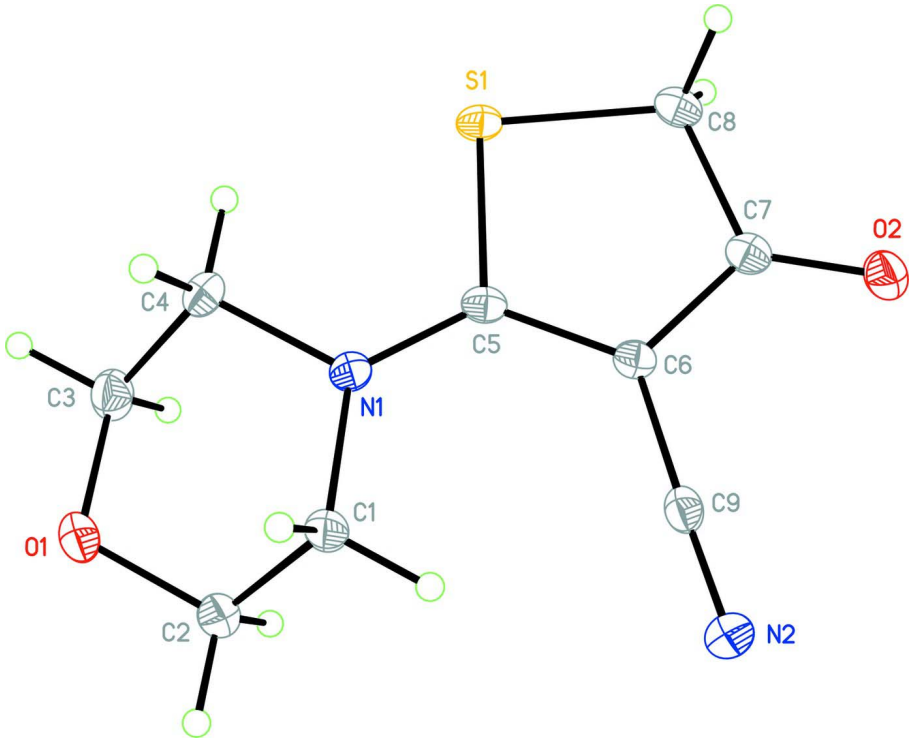

Figure 1

Molecular structure of the title compound, showing 50% probability displacement ellipsoids and atom numbering scheme. H atoms are drawn as circles with arbitrary small radius.

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Crystal data

$C_9H_{10}N_2O_2S$
$M_r = 210.25$
Monoclinic, $P2_1/c$
Hall symbol: -P 2ybc
$a = 7.1931\ (3)$ Å
$b = 17.3275\ (8)$ Å
$c = 7.2793\ (3)$ Å
$\beta = 94.506\ (2)°$
$V = 904.48\ (7)$ Å^3
$Z = 4$
$F(000) = 440$
$D_x = 1.544$ Mg m^{-3}
Cu $K\alpha$ radiation, $\lambda = 1.54178$ Å
Cell parameters from 2017 reflections
$\theta = 8.0–49.4°$
$\mu = 2.98$ mm^{-1}
$T = 100$ K
Blade, colorless
0.41 × 0.20 × 0.08 mm

Data collection

Bruker Kappa APEXII diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
phi and ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2001)
$T_{min} = 0.765$, $T_{max} = 0.919$
7337 measured reflections
1607 independent reflections
1531 reflections with $I > 2\sigma(I)$
$R_{int} = 0.027$
$\theta_{max} = 68.3°$, $\theta_{min} = 5.1°$
$h = -7\rightarrow8$
$k = -20\rightarrow20$
$l = -6\rightarrow8$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.026$
$wR(F^2) = 0.068$
$S = 1.08$
1607 reflections
128 parameters
0 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0333P)^2 + 0.4P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.005$
$\Delta\rho_{max} = 0.29$ e Å^{-3}
$\Delta\rho_{min} = -0.20$ e Å^{-3}
Extinction correction: *SHELXL97* (Sheldrick, 2008), $Fc^*=kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Extinction coefficient: 0.0051 (4)

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.

Refinement. Refinement of F^2 against ALL reflections. The weighted *R*-factor *wR* and goodness of fit *S* are based on F^2, conventional *R*-factors *R* are based on *F*, with *F* set to zero for negative F^2. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating *R*-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. *R*-factors based on F^2 are statistically about twice as large as those based on *F*, and *R*- factors based on ALL data will be even larger.

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

	x	*y*	*z*	U_{iso}*/U_{eq}
S1	0.41531 (4)	0.190051 (19)	0.14477 (4)	0.01446 (13)
O1	0.93155 (14)	−0.01397 (6)	0.25143 (14)	0.0203 (2)
O2	0.60927 (14)	0.39685 (6)	0.22161 (14)	0.0206 (2)
N2	1.03469 (17)	0.30903 (7)	0.41842 (18)	0.0206 (3)
N1	0.72767 (15)	0.12491 (7)	0.28592 (16)	0.0153 (3)
C3	0.7576 (2)	−0.00224 (8)	0.1488 (2)	0.0202 (3)
H3A	0.6948	−0.0526	0.1261	0.024*
H3B	0.7789	0.0210	0.0281	0.024*
C4	0.63342 (19)	0.05034 (8)	0.2519 (2)	0.0186 (3)
H4A	0.5133	0.0583	0.1783	0.022*
H4B	0.6072	0.0263	0.3706	0.022*
C5	0.64590 (18)	0.19201 (8)	0.24689 (18)	0.0127 (3)
C6	0.71300 (18)	0.26741 (8)	0.27408 (17)	0.0132 (3)
C7	0.58227 (19)	0.32720 (8)	0.21546 (17)	0.0143 (3)
C9	0.89130 (19)	0.28941 (8)	0.35321 (18)	0.0147 (3)
C8	0.39555 (18)	0.29364 (8)	0.14293 (18)	0.0163 (3)
H8A	0.3622	0.3121	0.0159	0.020*
H8B	0.2968	0.3101	0.2218	0.020*
C2	1.0259 (2)	0.05782 (8)	0.2777 (2)	0.0204 (3)
H2A	1.0490	0.0799	0.1562	0.025*
H2B	1.1482	0.0491	0.3468	0.025*
C1	0.91428 (19)	0.11467 (8)	0.3821 (2)	0.0191 (3)
H1A	0.9019	0.0954	0.5086	0.023*

H1B	0.9799	0.1649	0.3912	0.023*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.01039 (19)	0.0182 (2)	0.0144 (2)	−0.00046 (11)	−0.00152 (13)	−0.00068 (11)
O1	0.0208 (5)	0.0133 (5)	0.0264 (5)	0.0025 (4)	−0.0004 (4)	0.0007 (4)
O2	0.0198 (5)	0.0151 (5)	0.0270 (5)	0.0026 (4)	0.0030 (4)	0.0025 (4)
N2	0.0156 (6)	0.0184 (6)	0.0273 (7)	−0.0014 (5)	−0.0015 (5)	−0.0033 (5)
N1	0.0123 (5)	0.0139 (6)	0.0191 (6)	−0.0009 (4)	−0.0025 (5)	−0.0008 (4)
C3	0.0230 (8)	0.0154 (7)	0.0216 (7)	−0.0006 (5)	−0.0021 (6)	−0.0011 (5)
C4	0.0162 (7)	0.0139 (7)	0.0253 (7)	−0.0039 (5)	−0.0008 (6)	−0.0010 (5)
C5	0.0111 (6)	0.0169 (7)	0.0102 (6)	0.0006 (5)	0.0018 (5)	−0.0011 (5)
C6	0.0118 (6)	0.0149 (7)	0.0129 (6)	0.0007 (5)	0.0014 (5)	−0.0003 (5)
C7	0.0142 (6)	0.0174 (7)	0.0118 (6)	0.0011 (5)	0.0040 (5)	0.0008 (5)
C9	0.0167 (7)	0.0116 (6)	0.0161 (6)	0.0015 (5)	0.0036 (5)	−0.0006 (5)
C8	0.0135 (7)	0.0193 (7)	0.0159 (7)	0.0031 (5)	−0.0001 (5)	0.0011 (5)
C2	0.0158 (7)	0.0160 (7)	0.0293 (8)	0.0006 (5)	0.0008 (6)	0.0049 (6)
C1	0.0147 (7)	0.0145 (7)	0.0267 (7)	0.0004 (5)	−0.0071 (6)	0.0005 (5)

Geometric parameters (Å, º)

S1—C5	1.7639 (13)	C4—H4B	0.9900
S1—C8	1.8004 (14)	C5—C6	1.4014 (18)
O1—C3	1.4204 (17)	C6—C9	1.4163 (18)
O1—C2	1.4227 (17)	C6—C7	1.4410 (18)
O2—C7	1.2227 (17)	C7—C8	1.5197 (18)
N2—C9	1.1523 (19)	C8—H8A	0.9900
N1—C5	1.3238 (17)	C8—H8B	0.9900
N1—C4	1.4710 (17)	C2—C1	1.513 (2)
N1—C1	1.4751 (17)	C2—H2A	0.9900
C3—C4	1.515 (2)	C2—H2B	0.9900
C3—H3A	0.9900	C1—H1A	0.9900
C3—H3B	0.9900	C1—H1B	0.9900
C4—H4A	0.9900		
C5—S1—C8	93.15 (6)	O2—C7—C6	126.92 (13)
C3—O1—C2	109.68 (10)	O2—C7—C8	121.60 (12)
C5—N1—C4	122.97 (11)	C6—C7—C8	111.48 (12)
C5—N1—C1	125.44 (11)	N2—C9—C6	178.37 (15)
C4—N1—C1	111.37 (11)	C7—C8—S1	108.17 (9)
O1—C3—C4	110.79 (11)	C7—C8—H8A	110.1
O1—C3—H3A	109.5	S1—C8—H8A	110.1
C4—C3—H3A	109.5	C7—C8—H8B	110.1
O1—C3—H3B	109.5	S1—C8—H8B	110.1
C4—C3—H3B	109.5	H8A—C8—H8B	108.4
H3A—C3—H3B	108.1	O1—C2—C1	111.75 (11)
N1—C4—C3	109.24 (11)	O1—C2—H2A	109.3

N1—C4—H4A	109.8	C1—C2—H2A	109.3
C3—C4—H4A	109.8	O1—C2—H2B	109.3
N1—C4—H4B	109.8	C1—C2—H2B	109.3
C3—C4—H4B	109.8	H2A—C2—H2B	107.9
H4A—C4—H4B	108.3	N1—C1—C2	109.81 (11)
N1—C5—C6	130.26 (12)	N1—C1—H1A	109.7
N1—C5—S1	117.43 (10)	C2—C1—H1A	109.7
C6—C5—S1	112.30 (10)	N1—C1—H1B	109.7
C5—C6—C9	126.81 (12)	C2—C1—H1B	109.7
C5—C6—C7	114.77 (12)	H1A—C1—H1B	108.2
C9—C6—C7	118.42 (12)		