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Morpholin-4-ium morpholine-4-carbodithioate

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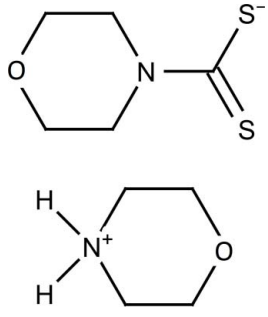
Key indicators: single-crystal X-ray study; T = 290 K; mean σ(C–C) = 0.005 Å; R factor = 0.050; wR factor = 0.145; data-to-parameter ratio = 18.4.

The title compound, $C_4H_{10}NO^+\cdot C_5H_8NOS_2^-$, is built up of a morpholinium cation and a dithiocarbamate anion. In the crystal, two structurally independent formula units are linked *via* N—H···S hydrogen bonds, forming an inversion dimer, with graph-set motif $R_4^4(12)$.

Related literature

For the crystal structures of similar compounds, see: Wahlberg (1979, 1980, 1981); Mafud & Gambardella (2011*a*,*b*). For graph-set analysis, see: Bernstein *et al.* (1995). For puckering parameters, see: Cremer & Pople (1975).



Experimental

Crystal data

$C_4H_{10}NO^+\cdot C_5H_8NOS_2^-$
M_r = 250.37
Monoclinic, $P2_1/c$
a = 7.938 (5) Å
b = 18.3232 (15) Å
c = 8.8260 (5) Å
β = 110.021 (5)°
V = 1206.2 (8) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.43 mm^{-1}
T = 290 K
0.3 × 0.15 × 0.15 mm

Data collection

Enraf–Nonius TurboCAD-4 diffractometer
Absorption correction: ψ scan (North *et al.*, 1968)
T_{min} = 0.795, T_{max} = 0.902
3705 measured reflections
3487 independent reflections
2021 reflections with $I > 2\sigma(I)$
R_{int} = 0.041
3 standard reflections every 120 min
intensity decay: 5%

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.050
$wR(F^2)$ = 0.145
S = 1.00
3487 reflections
190 parameters
All H-atom parameters refined
$\Delta\rho_{max}$ = 0.56 e Å^{-3}
$\Delta\rho_{min}$ = −0.39 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
N2—H1*N*···S1	0.86 (4)	2.47 (4)	3.284 (3)	158 (3)
N2—H2*N*···S1^{i}	0.91 (4)	2.75 (4)	3.453 (2)	135 (3)
N2—H2*N*···S2^{i}	0.91 (4)	2.39 (3)	3.221 (2)	151 (3)

Symmetry code: (i) $-x+1, -y, -z+2$.

Data collection: *CAD-4 EXPRESS* (Enraf–Nonius, 1989); cell refinement: *CAD-4 EXPRESS*; data reduction: *XCAD4* (Harms & Wocadlo, 1995); program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1994); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997) and *Mercury* (Macrae *et al.*, 2006); software used to prepare material for publication: *WinGX* (Farrugia, 1999), *PLATON* (Spek, 2009) and *publCIF* (Westrip, 2010).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: SU2285).

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supplementary materials

Acta Cryst. (2011). E**67**, o2008 [**doi:10.1107/S1600536811026286**]

Morpholin-4-ium morpholine-4-carbodithioate

A. C. Mafud, E. A. Sanches and M. T. Gambardella

Comment

The first thiocarbamic acid-ammonium salt, pyrrolidinedithiocarbamic acid-pyrrolidineammonium salt, was reported on previously by (Wahlberg, 1979; 1980; 1981). Our group have recently described the synthesis and crystal structures of ammonium piperidine-1-carbodithioate and sodium piperidine-1-carbodithioate dihydrate (Mafud & Gambardella, 2011*a*,*b*). Continuing our research on this subject, we report herein on the synthesis and crystal structure of the title salt, 1-Morpholinedithiocarbamic Acid-morpholineammonium Salt.

In the molecular structure of the title compound (Fig. 1) there is an intramolecular hydrogen bond involving the cation, via the nitrogen atom from amine group, and the anion, via the sulfur atom of dithiocarbamate (Table 1). The six membered rings have chair conformations, with puckering parameters are Q=0.554 (3) Å, θ = 177.4 (3)°, φ2 = 168 (6)° for the anion and Q = 0.566 (3) Å, θ = 1.4 (4)°, φ2 = 60 (14)° for the cation (Cremer & Pople, 1975).

In the crystal two structurally independent formula units are linked via N—H···S hydrogen bonds (Fig. 2, Table 1), to form a dimer arrangement centered about an inversion center, with graph-set $R^4_4(12)$ [Bernstein *et al.*, 1995].

Experimental

The RNH_2^+ salt of the morpholinedithiocarbamate was prepared by slow addition of 0.1 mol of CS_2 to a cold solution (ice bath) containing 0.2 mol of the morpholien amine dissolved in 30 ml of ethanol-water 1:1 (*v*/*v*) medium. The obtained solid was recrystallized from ethanol-water 1:1 (*v*/*v*) and dried in a vacuum oven at 323 K for 8 h. Colourless single crystals, suitable for X-ray diffraction analysis, were obtained. On heating they sublimed and decomposed.

Refinement

All H-atom positions were located in a difference Fourier map and were freely refined.

Figures

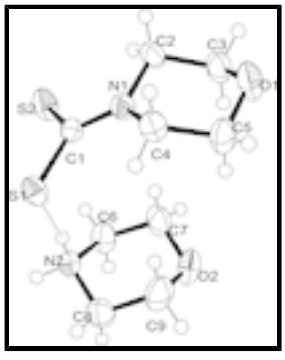

Fig. 1. Perspective view of the molecular structure of the title salt, with numering scheme and displacement ellipsoids drawn at the 50% probability level.

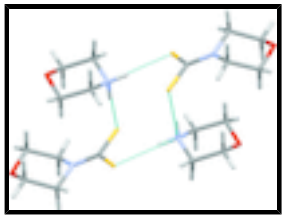

Fig. 2. Perspective view of the N-H···S hydrogen bonded (dashed cyan lines) dimer in the title salt, with graph-set $R^4_4(12)$.

Morpholin-4-ium morpholine-4-carbodithioate

Crystal data

$C_4H_{10}NO^+·C_5H_8NOS_2^-$	$F(000) = 536$
$M_r = 250.37$	$D_x = 1.379$ Mg m^{-3}
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Hall symbol: -P 2ybc	Cell parameters from 15 reflections
$a = 7.938$ (5) Å	$\theta = 5.5–15.9°$
$b = 18.3232$ (15) Å	$\mu = 0.43$ mm^{-1}
$c = 8.8260$ (5) Å	$T = 290$ K
$\beta = 110.021$ (5)°	Prism, colourless
$V = 1206.2$ (8) Å^3	0.3 × 0.15 × 0.15 mm
$Z = 4$	

Data collection

Enraf–Nonius TurboCAD-4 diffractometer	$R_{int} = 0.041$
graphite	$\theta_{max} = 30.0°$, $\theta_{min} = 2.7°$
non–profiled ω/2θ scans	$h = 0→11$
Absorption correction: ψ scan (North *et al.*, 1968)	$k = 0→25$
$T_{min} = 0.795$, $T_{max} = 0.902$	$l = -12→11$
3705 measured reflections	3 standard reflections every 120 min
3487 independent reflections	intensity decay: 5%
2021 reflections with $I > 2\sigma(I)$	

Refinement

Refinement on F^2	Primary atom site location: structure-invariant direct methods
Least-squares matrix: full	Secondary atom site location: difference Fourier map
$R[F^2 > 2\sigma(F^2)] = 0.050$	Hydrogen site location: inferred from neighbouring sites
$wR(F^2) = 0.145$	All H-atom parameters refined
$S = 1.00$	$w = 1/[\sigma^2(F_o^2) + (0.0759P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
3487 reflections	$(\Delta/\sigma)_{max} = 0.004$
190 parameters	$\Delta\rho_{max} = 0.56$ e Å^{-3}

0 restraints $\Delta\rho_{min} = -0.39$ 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.

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	0.20657 (9)	0.07843 (4)	0.84253 (7)	0.03827 (19)
S2	0.34115 (10)	−0.02991 (4)	0.66044 (8)	0.0448 (2)
O2	0.7186 (3)	0.20279 (12)	0.8050 (3)	0.0558 (5)
O1	0.1390 (3)	0.19488 (11)	0.2852 (2)	0.0547 (6)
N1	0.1685 (3)	0.09147 (11)	0.5323 (2)	0.0344 (5)
N2	0.6455 (3)	0.09075 (12)	0.9933 (3)	0.0352 (5)
C1	0.2314 (3)	0.04987 (13)	0.6648 (3)	0.0301 (5)
C2	0.1739 (4)	0.06872 (15)	0.3746 (3)	0.0425 (6)
C3	0.2422 (4)	0.13083 (16)	0.2981 (4)	0.0458 (7)
C4	0.0698 (4)	0.15994 (15)	0.5227 (3)	0.0390 (6)
C5	0.1441 (5)	0.21801 (15)	0.4412 (4)	0.0472 (7)
C6	0.7585 (5)	0.07751 (17)	0.8933 (4)	0.0478 (7)
C7	0.7033 (5)	0.12905 (18)	0.7531 (4)	0.0506 (7)
C8	0.6555 (5)	0.16802 (17)	1.0443 (4)	0.0515 (7)
C9	0.6074 (5)	0.21637 (17)	0.8988 (4)	0.0556 (8)
H1N	0.537 (5)	0.079 (2)	0.936 (4)	0.067*
H2N	0.681 (4)	0.063 (2)	1.085 (4)	0.067*
H2A	0.050 (4)	0.053 (2)	0.304 (4)	0.067*
H2B	0.248 (4)	0.027 (2)	0.394 (4)	0.067*
H3A	0.368 (4)	0.1441 (19)	0.369 (4)	0.067*
H3B	0.229 (4)	0.1177 (19)	0.187 (4)	0.067*
H4A	−0.053 (5)	0.1527 (19)	0.457 (4)	0.067*
H4B	0.088 (5)	0.1751 (18)	0.628 (4)	0.067*
H5A	0.274 (5)	0.2265 (19)	0.512 (4)	0.067*
H5B	0.073 (4)	0.261 (2)	0.419 (4)	0.067*
H6A	0.887 (5)	0.0884 (19)	0.966 (4)	0.067*
H6B	0.748 (4)	0.031 (2)	0.863 (4)	0.067*
H7A	0.582 (5)	0.1189 (19)	0.685 (4)	0.067*
H7B	0.786 (4)	0.125 (2)	0.697 (4)	0.067*
H8A	0.791 (5)	0.1709 (19)	1.118 (4)	0.067*
H8B	0.590 (5)	0.1737 (19)	1.108 (4)	0.067*

H9A	0.481 (5)	0.2048 (19)	0.826 (4)	0.067*
H9B	0.628 (5)	0.265 (2)	0.933 (4)	0.067*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.0437 (4)	0.0446 (4)	0.0318 (3)	0.0029 (3)	0.0197 (3)	0.0001 (3)
S2	0.0620 (5)	0.0378 (4)	0.0438 (4)	0.0134 (3)	0.0300 (3)	0.0079 (3)
O2	0.0626 (14)	0.0449 (12)	0.0676 (13)	−0.0052 (10)	0.0324 (11)	0.0156 (10)
O1	0.0774 (15)	0.0474 (12)	0.0479 (11)	0.0132 (10)	0.0324 (10)	0.0173 (9)
N1	0.0462 (13)	0.0290 (10)	0.0307 (10)	0.0011 (8)	0.0165 (9)	0.0002 (8)
N2	0.0395 (12)	0.0350 (11)	0.0336 (10)	−0.0027 (9)	0.0157 (9)	0.0043 (8)
C1	0.0302 (11)	0.0313 (11)	0.0309 (11)	−0.0057 (9)	0.0131 (9)	−0.0006 (9)
C2	0.0670 (19)	0.0366 (14)	0.0269 (12)	−0.0020 (13)	0.0199 (12)	−0.0014 (10)
C3	0.0606 (19)	0.0446 (16)	0.0388 (14)	0.0013 (14)	0.0254 (13)	0.0046 (12)
C4	0.0445 (16)	0.0373 (14)	0.0382 (13)	0.0062 (11)	0.0180 (12)	0.0031 (11)
C5	0.0602 (19)	0.0332 (14)	0.0537 (17)	0.0073 (13)	0.0267 (14)	0.0094 (12)
C6	0.0612 (19)	0.0389 (15)	0.0571 (17)	0.0089 (14)	0.0379 (15)	0.0054 (13)
C7	0.0625 (19)	0.0549 (18)	0.0460 (16)	−0.0029 (15)	0.0336 (15)	0.0057 (13)
C8	0.071 (2)	0.0428 (16)	0.0476 (16)	0.0035 (14)	0.0285 (15)	−0.0029 (12)
C9	0.071 (2)	0.0342 (15)	0.069 (2)	0.0078 (15)	0.0329 (17)	0.0062 (14)

Geometric parameters (Å, °)

S1—C1	1.728 (2)	C3—H3B	0.98 (4)
S2—C1	1.709 (2)	C4—C5	1.512 (4)
O2—C7	1.418 (4)	C4—H4A	0.96 (3)
O2—C9	1.423 (4)	C4—H4B	0.93 (3)
O1—C3	1.414 (3)	C5—H5A	1.02 (3)
O1—C5	1.428 (3)	C5—H5B	0.94 (4)
N1—C1	1.341 (3)	C6—C7	1.498 (4)
N1—C4	1.466 (3)	C6—H6A	1.02 (3)
N1—C2	1.468 (3)	C6—H6B	0.89 (4)
N2—C6	1.478 (3)	C7—H7A	0.96 (3)
N2—C8	1.480 (4)	C7—H7B	0.95 (4)
N2—H1N	0.86 (4)	C8—C9	1.498 (4)
N2—H2N	0.91 (4)	C8—H8A	1.05 (3)
C2—C3	1.515 (4)	C8—H8B	0.90 (3)
C2—H2A	1.01 (3)	C9—H9A	1.01 (3)
C2—H2B	0.94 (4)	C9—H9B	0.94 (4)
C3—H3A	1.01 (3)		
C7—O2—C9	110.7 (2)	H4A—C4—H4B	115 (3)
C3—O1—C5	110.1 (2)	O1—C5—C4	111.3 (2)
C1—N1—C4	124.7 (2)	O1—C5—H5A	108.8 (19)
C1—N1—C2	122.8 (2)	C4—C5—H5A	107.2 (19)
C4—N1—C2	112.2 (2)	O1—C5—H5B	103 (2)
C6—N2—C8	111.0 (2)	C4—C5—H5B	112 (2)
C6—N2—H1N	107 (2)	H5A—C5—H5B	114 (3)

C8—N2—H1N	111 (2)	N2—C6—C7	108.9 (2)
C6—N2—H2N	112 (2)	N2—C6—H6A	106.0 (19)
C8—N2—H2N	107 (2)	C7—C6—H6A	109.9 (19)
H1N—N2—H2N	109 (3)	N2—C6—H6B	109 (2)
N1—C1—S2	120.49 (17)	C7—C6—H6B	113 (2)
N1—C1—S1	119.70 (18)	H6A—C6—H6B	110 (3)
S2—C1—S1	119.79 (13)	O2—C7—C6	111.4 (3)
N1—C2—C3	109.9 (2)	O2—C7—H7A	110 (2)
N1—C2—H2A	109.1 (19)	C6—C7—H7A	110 (2)
C3—C2—H2A	111 (2)	O2—C7—H7B	104 (2)
N1—C2—H2B	106 (2)	C6—C7—H7B	109 (2)
C3—C2—H2B	113 (2)	H7A—C7—H7B	112 (3)
H2A—C2—H2B	108 (3)	N2—C8—C9	109.5 (2)
O1—C3—C2	111.9 (2)	N2—C8—H8A	100.0 (19)
O1—C3—H3A	106 (2)	C9—C8—H8A	114.1 (19)
C2—C3—H3A	109.6 (19)	N2—C8—H8B	109 (2)
O1—C3—H3B	105 (2)	C9—C8—H8B	116 (2)
C2—C3—H3B	109 (2)	H8A—C8—H8B	107 (3)
H3A—C3—H3B	115 (3)	O2—C9—C8	111.6 (3)
N1—C4—C5	110.0 (2)	O2—C9—H9A	105.6 (19)
N1—C4—H4A	109 (2)	C8—C9—H9A	109.2 (19)
C5—C4—H4A	107 (2)	O2—C9—H9B	106 (2)
N1—C4—H4B	107 (2)	C8—C9—H9B	109 (2)
C5—C4—H4B	108 (2)	H9A—C9—H9B	116 (3)
C4—N1—C1—S2	178.8 (2)	C2—N1—C4—C5	−53.1 (3)
C2—N1—C1—S2	5.9 (3)	C3—O1—C5—C4	−60.0 (3)
C4—N1—C1—S1	−3.0 (3)	N1—C4—C5—O1	56.4 (3)
C2—N1—C1—S1	−175.9 (2)	C8—N2—C6—C7	−55.7 (4)
C1—N1—C2—C3	−133.9 (3)	C9—O2—C7—C6	−60.0 (4)
C4—N1—C2—C3	52.4 (3)	N2—C6—C7—O2	58.1 (4)
C5—O1—C3—C2	59.7 (3)	C6—N2—C8—C9	54.9 (4)
N1—C2—C3—O1	−55.7 (3)	C7—O2—C9—C8	59.0 (4)
C1—N1—C4—C5	133.4 (3)	N2—C8—C9—O2	−56.2 (4)

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N2—H1N···S1	0.86 (4)	2.47 (4)	3.284 (3)	158 (3)
N2—H2N···S1^{i}	0.91 (4)	2.75 (4)	3.453 (2)	135 (3)
N2—H2N···S2^{i}	0.91 (4)	2.39 (3)	3.221 (2)	151 (3)

Symmetry codes: (i) −*x*+1, −*y*, −*z*+2.

Fig. 1

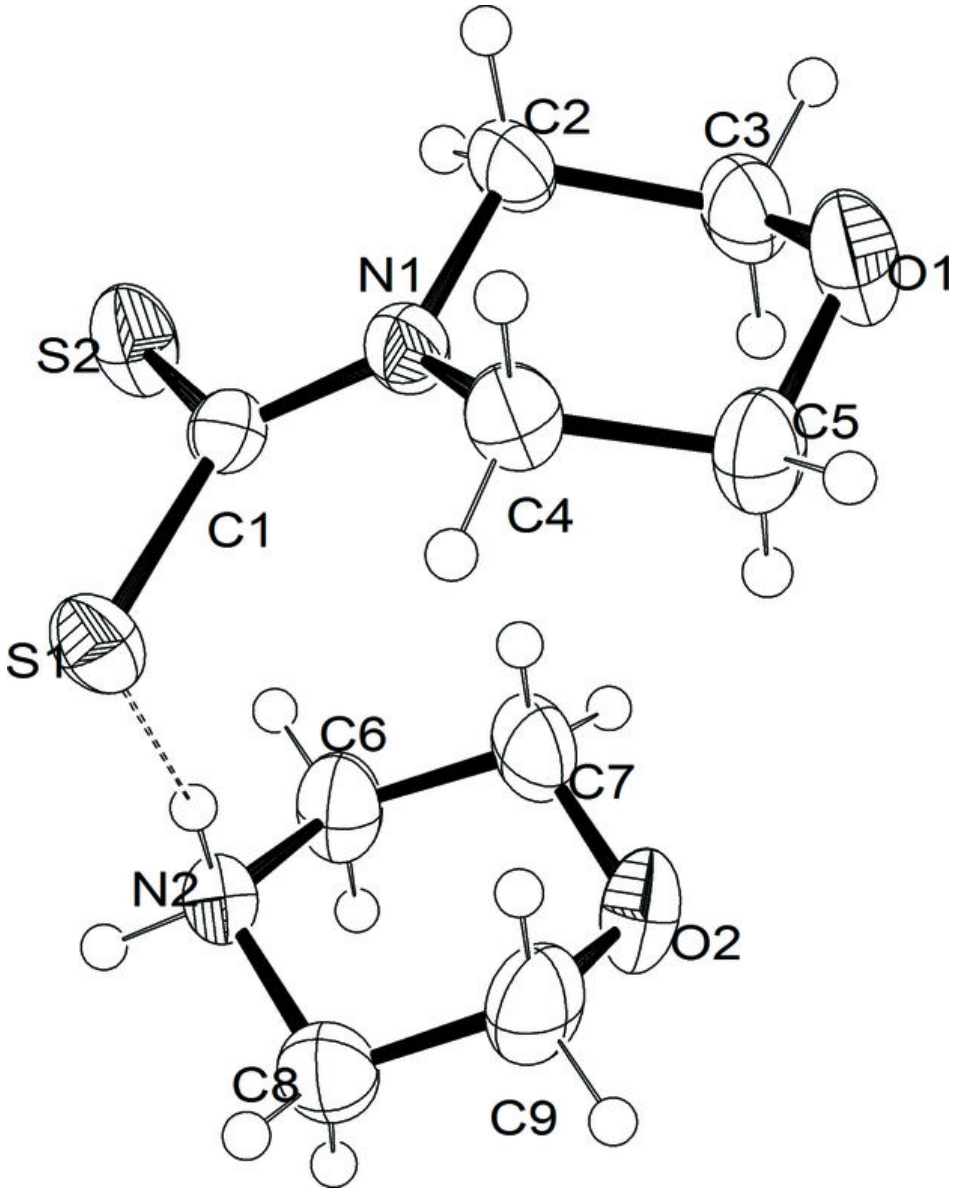

Fig. 2