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2-(4-Morpholinecarbothioylsulfanyl)-acetic acid

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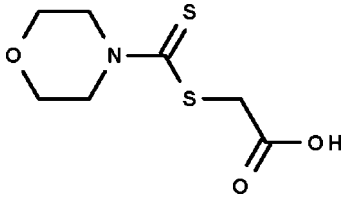
Key indicators: single-crystal X-ray study; T = 293 K; mean σ(C–C) = 0.009 Å; R factor = 0.066; wR factor = 0.188; data-to-parameter ratio = 19.0.

The asymmetric unit of the title compound, $C_7H_{11}NO_3S_2$, contains two independent molecules with similar molecular structures. The morpholine ring adopts a chair conformation, and the $C_2N-C(=S)-S$ fragment is planar in the two independent molecules (r.m.s. deviations = 0.01 and 0.02 Å). The two molecules are disposed about a false center of inversion and are held together by a pair of O—H···O hydrogen bonds. The crystal studied was a racemic twin; the minor twin component refined to 17%.

Related literature

For the hydrogen-bonded dicyclohexylammonium salt, see: Ng & Hook (1999). For the synthesis, see: Nachmias (1952).



Experimental

Crystal data

$C_7H_{11}NO_3S_2$
M_r = 221.29
Orthorhombic, $Pca2_1$
a = 14.7311 (3) Å
b = 4.7474 (1) Å
c = 28.0284 (5) Å
V = 1960.15 (7) Å^3
Z = 8
Mo $K\alpha$ radiation
μ = 0.52 mm^{-1}
T = 293 K
0.20 × 0.20 × 0.20 mm

Data collection

Bruker SMART APEX diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
T_{min} = 0.904, T_{max} = 0.904
16961 measured reflections
4495 independent reflections
3533 reflections with $I > 2\sigma(I)$
R_{int} = 0.060

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.066
$wR(F^2)$ = 0.188
S = 1.11
4495 reflections
236 parameters
5 restraints
H-atom parameters constrained
$\Delta\rho_{max}$ = 1.52 e Å^{-3}
$\Delta\rho_{min}$ = −0.37 e Å^{-3}
Absolute structure: Flack (1983), 2199 Friedel pairs
Flack parameter: 0.2 (1)

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

D—H···A	D—H	H···A	D···A	D—H···A
O1—H1···O5	0.82	1.88	2.685 (7)	169
O4—H4···O2	0.82	1.88	2.689 (7)	170

Data collection: *APEX2* (Bruker, 2009); cell refinement: *SAINT* (Bruker, 2009); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *X-SEED* (Barbour, 2001); software used to prepare material for publication: *pubCIF* (Westrip, 2010).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: XU2747).

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supporting information

Acta Cryst. (2010). E**66**, o1078 [https://doi.org/10.1107/S1600536810012602]

2-(4-Morpholinecarbothioylsulfanyl)acetic acid

Kong Mun Lo and Seik Weng Ng

S1. Comment

The class of dithiocarbamyl-acetic acids, $R_2NC(S)SCH_2CO_2H$, are synthetic plant growth-hormones. In an earlier study, the $R_2N = O(CH_2CH_2)_2N$ derivative was characterized as the dicyclohexylammonium salt (Ng & Hook, 1999). The acid itself (Scheme I), exists as a hydrogen-bonded dimer, the two independent molecules being connected across a false center-of-inversion (Fig. 1, Table 1). The carboxyl $–CO_2$ portions feature single as well as double carbon-oxygen bonds.

S2. Experimental

The carboxylic acid was synthesized from morpholine, carbon disulfide and chloroacetic acid (Nachmias, 1952), and was recrystallized from ethanol.

S3. Refinement

The carbon-carbon distances in the morpholine rings were retraied to 1.54±0.01 Å.

Hydrogen atoms were placed at calculated positions (C–H 0.97, O–H 0.82 Å) and were treated as riding on their parent atoms, with U(H) set to 1.2–1.5 times U_{eq}(C,O). The final difference Fourier map had a peak 2.2 Å from S2.

The crystal is a racemic twin; the minor twin component refined to 17%.

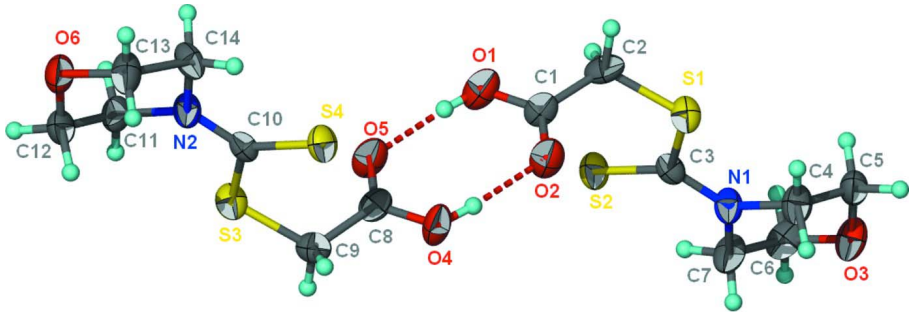

Figure 1

Thermal ellipsoid plot (Barbour, 2001) of the pair of $C_7H_{11}NO_3S_2$ molecules disposed about a false center-of-inversion at the 50% probability level. H atoms are drawn as spheres of arbitrary radius.

2-(4-Morpholinecarbothioylsulfanyl)acetic acid

Crystal data

$C_7H_{11}NO_3S_2$
$M_r = 221.29$
Orthorhombic, $Pca2_1$
Hall symbol: P 2c -2ac
$a = 14.7311$ (3) Å
$b = 4.7474$ (1) Å
$c = 28.0284$ (5) Å
$V = 1960.15$ (7) Å^3
$Z = 8$
$F(000) = 928$

D_x = 1.500 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 3880 reflections
θ = 2.9–25.7°
μ = 0.52 mm^{-1}
T = 293 K
Block, colorless
0.20 × 0.20 × 0.20 mm

Data collection

Bruker SMART APEX diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
T_{min} = 0.904, T_{max} = 0.904
16961 measured reflections
4495 independent reflections
3533 reflections with $I > 2\sigma(I)$
R_{int} = 0.060
θ_{max} = 27.5°, θ_{min} = 1.5°
h = −19→19
k = −6→6
l = −36→36

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.066
$wR(F^2)$ = 0.188
S = 1.11
4495 reflections
236 parameters
5 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
$w = 1/[\sigma^2(F_o^2) + (0.1026P)^2 + 0.7215P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 1.52 e Å^{-3}
$\Delta\rho_{min}$ = −0.37 e Å^{-3}
Absolute structure: Flack (1983), 2199 Friedel pairs
Absolute structure parameter: 0.2 (1)

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

	x	*y*	*z*	U_{iso}*/U_{eq}
S1	1.14478 (11)	0.9468 (4)	0.50019 (5)	0.0443 (3)
S2	0.99909 (9)	0.7699 (3)	0.43159 (7)	0.0498 (3)
S3	0.60753 (11)	0.5544 (4)	0.64749 (5)	0.0461 (4)
S4	0.75227 (9)	0.7362 (3)	0.71543 (6)	0.0482 (3)
O1	0.8902 (4)	1.0465 (12)	0.5349 (2)	0.0628 (15)
H1	0.8469	0.9640	0.5468	0.094*
O2	0.9876 (3)	0.7466 (9)	0.56506 (17)	0.0592 (12)
O3	1.3067 (4)	0.5162 (10)	0.3578 (2)	0.0561 (15)
O4	0.8628 (3)	0.4614 (10)	0.6158 (2)	0.0575 (14)
H4	0.9054	0.5431	0.6030	0.086*
O5	0.7633 (3)	0.7541 (9)	0.58260 (16)	0.0596 (12)
O6	0.4379 (4)	0.9934 (10)	0.7892 (3)	0.0605 (16)
N1	1.1727 (3)	0.6195 (11)	0.42631 (16)	0.0446 (11)
N2	0.5791 (3)	0.8762 (10)	0.72174 (16)	0.0439 (10)
C1	0.9717 (5)	0.9533 (15)	0.5416 (2)	0.0475 (16)
C2	1.0451 (4)	1.1257 (11)	0.5176 (2)	0.0510 (13)
H2A	1.0624	1.2764	0.5392	0.061*
H2B	1.0190	1.2126	0.4895	0.061*
C3	1.1053 (3)	0.7611 (10)	0.44898 (18)	0.0363 (10)

C4	1.2672 (4)	0.6143 (15)	0.4401 (2)	0.0527 (14)
H4A	1.2835	0.4266	0.4507	0.063*
H4B	1.2770	0.7439	0.4663	0.063*
C5	1.3265 (4)	0.6978 (12)	0.3981 (2)	0.0533 (14)
H5A	1.3149	0.8925	0.3895	0.064*
H5B	1.3900	0.6805	0.4068	0.064*
C6	1.2189 (5)	0.5326 (16)	0.3440 (2)	0.055 (2)
H6A	1.2094	0.4105	0.3168	0.066*
H6B	1.2055	0.7241	0.3343	0.066*
C7	1.1559 (5)	0.4494 (18)	0.3830 (3)	0.061 (2)
H7A	1.0937	0.4761	0.3726	0.073*
H7B	1.1642	0.2514	0.3903	0.073*
C8	0.7808 (5)	0.5473 (14)	0.6087 (2)	0.0425 (14)
C9	0.7074 (4)	0.3719 (11)	0.63020 (19)	0.0452 (12)
H9A	0.7320	0.2777	0.6581	0.054*
H9B	0.6906	0.2272	0.6074	0.054*
C10	0.6437 (3)	0.7404 (10)	0.69901 (17)	0.0348 (10)
C11	0.4816 (3)	0.8793 (13)	0.7084 (2)	0.0486 (13)
H11A	0.4704	0.7443	0.6831	0.058*
H11B	0.4646	1.0649	0.6970	0.058*
C12	0.4262 (4)	0.8035 (13)	0.7521 (2)	0.0528 (14)
H12A	0.3625	0.7975	0.7434	0.063*
H12B	0.4436	0.6170	0.7628	0.063*
C13	0.5344 (5)	0.9823 (16)	0.8041 (3)	0.056 (2)
H13A	0.5481	0.7961	0.8163	0.067*
H13B	0.5445	1.1172	0.8295	0.067*
C14	0.5974 (4)	1.0483 (14)	0.7627 (2)	0.0462 (15)
H14A	0.5907	1.2449	0.7540	0.055*
H14B	0.6597	1.0191	0.7727	0.055*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.0386 (8)	0.0618 (7)	0.0325 (7)	−0.0035 (7)	−0.0021 (6)	−0.0066 (9)
S2	0.0345 (6)	0.0625 (9)	0.0525 (7)	−0.0025 (6)	−0.0064 (5)	−0.0034 (6)
S3	0.0434 (8)	0.0601 (7)	0.0348 (7)	−0.0063 (7)	−0.0038 (6)	−0.0045 (9)
S4	0.0357 (6)	0.0615 (8)	0.0476 (6)	−0.0024 (6)	−0.0059 (6)	0.0009 (6)
O1	0.061 (3)	0.071 (3)	0.056 (3)	0.023 (3)	0.011 (3)	0.006 (2)
O2	0.055 (3)	0.065 (3)	0.058 (2)	0.013 (2)	0.009 (2)	0.020 (2)
O3	0.047 (3)	0.083 (4)	0.039 (3)	0.013 (2)	0.013 (3)	−0.0063 (18)
O4	0.044 (3)	0.069 (3)	0.059 (3)	0.019 (2)	0.013 (2)	0.028 (2)
O5	0.061 (3)	0.060 (3)	0.058 (3)	0.020 (2)	0.012 (2)	0.028 (2)
O6	0.034 (3)	0.069 (4)	0.078 (4)	0.0018 (17)	0.000 (3)	−0.011 (2)
N1	0.032 (2)	0.061 (3)	0.041 (2)	−0.003 (2)	−0.0004 (18)	−0.011 (2)
N2	0.032 (2)	0.056 (3)	0.043 (3)	−0.002 (2)	−0.0055 (18)	−0.010 (2)
C1	0.054 (4)	0.050 (3)	0.039 (3)	0.012 (3)	0.003 (3)	0.013 (3)
C2	0.073 (4)	0.039 (3)	0.041 (3)	0.011 (3)	0.004 (3)	−0.006 (2)
C3	0.037 (3)	0.040 (3)	0.032 (2)	−0.0069 (19)	−0.0011 (17)	0.003 (2)

C4	0.042 (3)	0.069 (4)	0.048 (3)	0.002 (3)	−0.003 (2)	−0.004 (3)
C5	0.036 (3)	0.051 (3)	0.073 (4)	0.004 (2)	0.006 (3)	0.008 (3)
C6	0.064 (5)	0.069 (4)	0.033 (4)	0.011 (3)	−0.002 (3)	−0.012 (3)
C7	0.044 (4)	0.073 (4)	0.066 (5)	0.004 (3)	−0.005 (3)	−0.036 (4)
C8	0.050 (4)	0.049 (3)	0.028 (3)	0.005 (3)	0.006 (2)	−0.009 (2)
C9	0.056 (3)	0.040 (3)	0.039 (3)	−0.005 (3)	0.005 (2)	0.001 (2)
C10	0.036 (2)	0.040 (3)	0.029 (2)	−0.0089 (19)	−0.0042 (18)	0.007 (2)
C11	0.030 (2)	0.062 (4)	0.053 (3)	0.006 (3)	−0.011 (2)	−0.006 (3)
C12	0.031 (3)	0.053 (3)	0.074 (4)	−0.003 (2)	−0.003 (2)	0.003 (3)
C13	0.037 (4)	0.080 (5)	0.051 (5)	0.003 (3)	0.000 (3)	−0.005 (3)
C14	0.044 (3)	0.058 (3)	0.037 (3)	−0.015 (3)	0.007 (3)	−0.009 (3)

Geometric parameters (Å, º)

S1—C2	1.765 (6)	C2—H2B	0.9700
S1—C3	1.782 (5)	C4—C5	1.518 (7)
S2—C3	1.640 (5)	C4—H4A	0.9700
S3—C10	1.774 (5)	C4—H4B	0.9700
S3—C9	1.775 (6)	C5—H5A	0.9700
S4—C10	1.664 (5)	C5—H5B	0.9700
O1—C1	1.294 (8)	C6—C7	1.487 (8)
O1—H1	0.8200	C6—H6A	0.9700
O2—C1	1.204 (8)	C6—H6B	0.9700
O3—C6	1.352 (10)	C7—H7A	0.9700
O3—C5	1.450 (9)	C7—H7B	0.9700
O4—C8	1.291 (8)	C8—C9	1.492 (9)
O4—H4	0.8200	C9—H9A	0.9700
O5—C8	1.251 (8)	C9—H9B	0.9700
O6—C12	1.387 (8)	C11—C12	1.514 (7)
O6—C13	1.481 (10)	C11—H11A	0.9700
N1—C3	1.357 (7)	C11—H11B	0.9700
N1—C4	1.444 (7)	C12—H12A	0.9700
N1—C7	1.479 (8)	C12—H12B	0.9700
N2—C10	1.314 (7)	C13—C14	1.519 (7)
N2—C14	1.434 (8)	C13—H13A	0.9700
N2—C11	1.484 (6)	C13—H13B	0.9700
C1—C2	1.514 (9)	C14—H14A	0.9700
C2—H2A	0.9700	C14—H14B	0.9700
C2—S1—C3	100.9 (3)	N1—C7—C6	110.7 (6)
C10—S3—C9	102.5 (3)	N1—C7—H7A	109.5
C1—O1—H1	120.0	C6—C7—H7A	109.5
C6—O3—C5	112.3 (5)	N1—C7—H7B	109.5
C8—O4—H4	120.0	C6—C7—H7B	109.5
C12—O6—C13	107.9 (5)	H7A—C7—H7B	108.1
C3—N1—C4	126.0 (4)	O5—C8—O4	122.1 (6)
C3—N1—C7	122.2 (5)	O5—C8—C9	121.7 (6)
C4—N1—C7	111.8 (5)	O4—C8—C9	116.1 (6)

C10—N2—C14	122.1 (4)	C8—C9—S3	116.0 (4)
C10—N2—C11	125.7 (4)	C8—C9—H9A	108.3
C14—N2—C11	112.2 (5)	S3—C9—H9A	108.3
O2—C1—O1	122.6 (7)	C8—C9—H9B	108.3
O2—C1—C2	123.0 (6)	S3—C9—H9B	108.3
O1—C1—C2	114.4 (6)	H9A—C9—H9B	107.4
C1—C2—S1	117.2 (4)	N2—C10—S4	124.6 (4)
C1—C2—H2A	108.0	N2—C10—S3	114.9 (4)
S1—C2—H2A	108.0	S4—C10—S3	120.5 (3)
C1—C2—H2B	108.0	N2—C11—C12	108.4 (4)
S1—C2—H2B	108.0	N2—C11—H11A	110.0
H2A—C2—H2B	107.2	C12—C11—H11A	110.0
N1—C3—S2	124.9 (4)	N2—C11—H11B	110.0
N1—C3—S1	112.6 (4)	C12—C11—H11B	110.0
S2—C3—S1	122.6 (3)	H11A—C11—H11B	108.4
N1—C4—C5	110.1 (5)	O6—C12—C11	112.6 (5)
N1—C4—H4A	109.6	O6—C12—H12A	109.1
C5—C4—H4A	109.6	C11—C12—H12A	109.1
N1—C4—H4B	109.6	O6—C12—H12B	109.1
C5—C4—H4B	109.6	C11—C12—H12B	109.1
H4A—C4—H4B	108.2	H12A—C12—H12B	107.8
O3—C5—C4	109.4 (5)	O6—C13—C14	111.3 (7)
O3—C5—H5A	109.8	O6—C13—H13A	109.4
C4—C5—H5A	109.8	C14—C13—H13A	109.4
O3—C5—H5B	109.8	O6—C13—H13B	109.4
C4—C5—H5B	109.8	C14—C13—H13B	109.4
H5A—C5—H5B	108.2	H13A—C13—H13B	108.0
O3—C6—C7	111.9 (6)	N2—C14—C13	112.3 (5)
O3—C6—H6A	109.2	N2—C14—H14A	109.2
C7—C6—H6A	109.2	C13—C14—H14A	109.2
O3—C6—H6B	109.2	N2—C14—H14B	109.2
C7—C6—H6B	109.2	C13—C14—H14B	109.1
H6A—C6—H6B	107.9	H14A—C14—H14B	107.9

O2—C1—C2—S1	29.1 (9)	O5—C8—C9—S3	−35.2 (8)
O1—C1—C2—S1	−150.9 (6)	O4—C8—C9—S3	149.5 (6)
C3—S1—C2—C1	74.8 (5)	C10—S3—C9—C8	−72.7 (5)
C4—N1—C3—S2	178.2 (5)	C14—N2—C10—S4	2.9 (7)
C7—N1—C3—S2	−1.4 (8)	C11—N2—C10—S4	−178.8 (4)
C4—N1—C3—S1	−0.7 (7)	C14—N2—C10—S3	−176.9 (4)
C7—N1—C3—S1	179.8 (5)	C11—N2—C10—S3	1.4 (7)
C2—S1—C3—N1	175.4 (4)	C9—S3—C10—N2	−174.2 (4)
C2—S1—C3—S2	−3.5 (4)	C9—S3—C10—S4	6.0 (4)
C3—N1—C4—C5	−126.6 (6)	C10—N2—C11—C12	128.6 (5)
C7—N1—C4—C5	53.0 (8)	C14—N2—C11—C12	−53.0 (7)
C6—O3—C5—C4	59.7 (7)	C13—O6—C12—C11	−63.0 (7)
N1—C4—C5—O3	−55.2 (7)	N2—C11—C12—O6	61.0 (7)
C5—O3—C6—C7	−60.0 (8)	C12—O6—C13—C14	57.6 (7)

C3—N1—C7—C6	127.4 (7)	C10—N2—C14—C13	−130.6 (6)
C4—N1—C7—C6	−52.2 (9)	C11—N2—C14—C13	50.9 (8)
O3—C6—C7—N1	55.3 (8)	O6—C13—C14—N2	−52.6 (8)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H1···O5	0.82	1.88	2.685 (7)	169
O4—H4···O2	0.82	1.88	2.689 (7)	170