Hydrogen-bond thio acceptors in O-methyl 3,4-dimethylpyrrole-2-thio-carboxylate

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Molecules of the title compound, $C_8H_{11}NOS$, are flat and almost C_s-symmetric. Bond lengths and angles resemble calculated values at the B3LYP/6-311+G(2 d,p) level of theory. The solid is characterized by van der Waals bonding and π stacking (stacking distance = 3.352 Å) of the basic motif of the structure: planar centrosymmetric dimers that are bonded by pairs of symmetry-equivalent N—H···S bonds. The dimer structure is rationalized by the nature of the hydrogen-bond acceptor orbital, the $S(3p)$ orbital located in the molecular plane. The double-donor–double-acceptor situation in the dimer results in an unusual C=S···H angle of about 127° which is large compared with isolated C=S···H bonds (circa 100°), but small compared with the almost linear acceptor geometry in related oxo compounds.

Related literature

The title compound was prepared according to a modified procedure as previously described by Plater et al. (2002). A recent analysis, including an identification of the acceptor lone pair and the considerable strength of hydrogen bonds to sulfur acceptors, has been published by Wennmohs et al. (2003), who use the non-bonding orbital method as the localization algorithm. The metric aspects of hydrogen bonding to C=S acceptors have been reviewed by Allen et al. (1997). The structure of a related dimer-forming oxo analogue has recently been reported by Ramos Silva et al. (2007). A related N—H···S=C-linked, but non-centrosymmetric, dimer has been found for a morpholine-dithione derivative (Linden et al., 2001). For related literature, see: Voet et al. (1999).
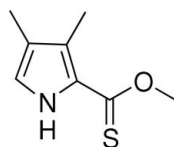
Experimental

Crystal data

$C_8H_{11}NOS$	V = 866.12 (4) Å^3
M_r = 169.24	Z = 4
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation
a = 7.4399 (2) Å	μ = 0.32 mm^{-1}
b = 13.9413 (5) Å	T = 200 (2) K
c = 8.4118 (2) Å	0.25 × 0.21 × 0.18 mm
β = 96.928 (2)°	

Data collection

Nonius KappaCCD diffractometer	1980 independent reflections
Absorption correction: none	1724 reflections with $I > 2\sigma(I)$
3806 measured reflections	R_{int} = 0.015

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.041	Only H-atom displacement
$wR(F^2)$ = 0.118	parameters refined
S = 1.10	$\Delta\rho_{max}$ = 0.33 e Å^{-3}
1980 reflections	$\Delta\rho_{min}$ = −0.28 e Å^{-3}
109 parameters	

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

D—H···A	D—H	H···A	D···A	D—H···A
N—H7···S^i	0.84 (2)	2.69 (2)	3.3622 (15)	138.7 (18)

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

Data collection: *COLLECT* (Nonius, 2004); cell refinement: *SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *SCALEPACK* and *DENZO* (Otwinowski & Minor, 1997); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEPIII* (Burnett & Johnson, 1996); software used to prepare material for publication: *SHELXL97*.

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supplementary materials

Hydrogen-bond thio acceptors in *O*-methyl 3,4-dimethylpyrrole-2-thiocarboxylate

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Comment

The title compound, $C_8H_{11}NOS$, was prepared as the parent acid of a potentially chelating ligand.

The flat molecules of the title compound combine to centrosymmetric dimers by means of two hydrogen bonds of the N—H···S=C type (Figure 2). The dimeric structure reflects the nature of the hydrogen-bond acceptor orbital at the sulfur atom: one of the sulfur lone pairs – the HOMO of the molecule which, in terms of an NBO analysis, exhibits S(3p) character – is the best suited acceptor orbital in terms of hydrogen-bond strength. This orbital lies in the molecular plane, perpendicular to the C=S axis. Almost flat dimers thus have to be expected with H···S=C angles close to 90°. Accordingly, the dimers are flat. The C=S···H angle, however, is unusually obtuse (127°) compared with the expectation values [approx. 90° from frontier-orbital considerations, approx. 100° as the experimental mean value, compare with Allen *et al.* (1997)]. The reason is the double-donor-double-acceptor situation in the dimer. The smaller the acceptor angle, the closer the repulsive N—H···H—N contact. The experimentally determined 127° angle is thus a compromise (note a somewhat different view on the dimer by counting the intramolecular H···S contact despite the small N—H···S angle of 108° as a hydrogen bond as well, ending up with bifurcated bonds). Though the acceptor angle is unusually large for a sulfur compound, it is much smaller than the acceptor angle in related oxo compounds due to the different acceptor-orbital situation in the oxo case (Ramos Silva *et al.*, 2007).

The packing of the dimers is determined by van-der-Waals forces. Figure 3 shows the stacking of the flat molecules. The normal distance of the molecular planes is 3.352 Å and thus resembles the typical 3.4-Å distance of π-stacked nucleic bases. However, the typical partial overlap of the DNA azaaromates (Voet *et al.*, 1999) is not observed in (I). Instead, a close perpendicular contact is found for a single ring atom only (C4). Figure 4 shows this situation in a normal view. The figure suggests that, possibly, the methyl groups prohibit a more extended π-stacking-type contact.

Experimental

The title compound, $C_8H_{11}NOS$, was prepared upon the reaction of thiophosgene with 3,3'-dimethylpyrrole in diethylether under ice cooling, subsequent heat up to room temperature, and quenching of the reaction products with methanol after 30 minutes' reaction time. Subsequent workup with column chromatography on silica with chloroform as the mobile phase yielded pale yellow crystals. Sublimation of the raw product yielded colourless crystals of the title compound.

Refinement

All H atoms were located in a difference map. C-bonded H atoms were refined as riding on their parent atoms. One common isotropic displacement parameter for the methyl-H atoms was refined, individual U values were refined for the methylidine-H and the N-bonded H. The positional parameters of the N-bonded H atom were refined freely.
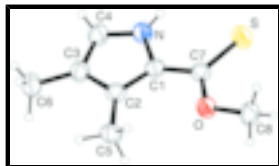
supplementary materials

Figures

Fig. 1. The molecular structure of (I), with atom labels and anisotropic displacement ellipsoids (drawn at 50% probability level) for non-H atoms.
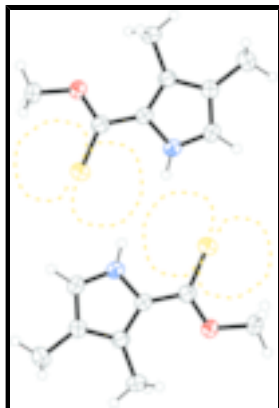

Fig. 2. N—H···S-bonded dimers. The contour of the S(3p) acceptor orbital from an NBO analysis on a single molecule of (I) is drawn at an isovalue of 0.02.
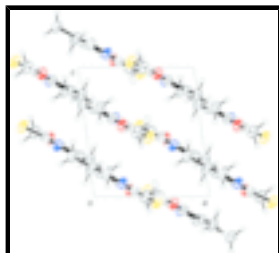

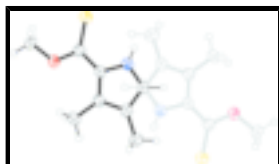Fig. 3. π stacking along [101], projected down [0 1 0].

Fig. 4. Closest contact of the aromatic rings in a centrosymmetric pair of molecules of adjacent stacks in a normal view.

O-methyl 3,4-dimethylpyrrole-2-thiocarboxylate

Crystal data

$C_8H_{11}NOS$	$F_{000} = 360$
$M_r = 169.24$	$D_x = 1.298$ Mg m^{-3}
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation $\lambda = 0.71073$ Å
Hall symbol: -P 2ybc	Cell parameters from 15311 reflections
$a = 7.4399$ (2) Å	$\theta = 3.1–27.5°$
$b = 13.9413$ (5) Å	$\mu = 0.32$ mm^{-1}
$c = 8.4118$ (2) Å	$T = 200$ (2) K
$\beta = 96.928$ (2)°	Block, colourless
$V = 866.12$ (4) Å^3	$0.25 \times 0.21 \times 0.18$ mm
$Z = 4$	

Data collection

Nonius KappaCCD diffractometer	1724 reflections with $I > 2\sigma(I)$
Radiation source: rotating anode	$R_{int} = 0.015$
Monochromator: MONTEL, graded multilayered X-ray optics	$\theta_{max} = 27.5^\circ$
$T = 200(2)$ K	$\theta_{min} = 3.8^\circ$
CCD; rotation images; thick slices scans	$h = -9 \rightarrow 9$
Absorption correction: none	$k = -18 \rightarrow 17$
3806 measured reflections	$l = -10 \rightarrow 10$
1980 independent reflections	

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.041$	Only H-atom displacement parameters refined
$wR(F^2) = 0.118$	$w = 1/[\sigma^2(F_o^2) + (0.0618P)^2 + 0.2807P]$ where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.10$	$(\Delta/\sigma)_{max} < 0.001$
1980 reflections	$\Delta\rho_{max} = 0.33$ e Å^{-3}
109 parameters	$\Delta\rho_{min} = -0.28$ e Å^{-3}
Primary atom site location: structure-invariant direct methods	Extinction correction: none

Special details

Refinement. the refU entry for H-atom refinement summarizes: individual U for the single C-bonded H, one common U for the methyl-Hs. All H-atom parameters refined for the N-bonded H.

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

	x	y	z	U_{iso}*/U_{eq}
S	0.45898 (6)	0.33388 (3)	0.54208 (6)	0.04671 (18)
O	0.68081 (15)	0.20285 (8)	0.44864 (14)	0.0402 (3)
N	0.73885 (19)	0.45490 (10)	0.39510 (17)	0.0379 (3)
H7	0.658 (3)	0.4848 (15)	0.435 (3)	0.048 (6)*
C1	0.7642 (2)	0.35680 (11)	0.39575 (18)	0.0324 (3)
C2	0.9182 (2)	0.33903 (10)	0.31993 (18)	0.0329 (3)
C3	0.9836 (2)	0.42870 (11)	0.27372 (19)	0.0367 (3)
C4	0.8693 (2)	0.49803 (12)	0.3232 (2)	0.0408 (4)
H4	0.8810	0.5652	0.3087	0.054 (6)*
C5	1.0016 (2)	0.24411 (12)	0.2895 (2)	0.0405 (4)
H51	0.9072	0.1997	0.2434	0.097 (3)*
H52	1.0608	0.2179	0.3906	0.097 (3)*

H53	1.0915	0.2525	0.2145	0.097 (3)*
C6	1.1463 (2)	0.44705 (14)	0.1889 (2)	0.0482 (4)
H61	1.1655	0.5163	0.1810	0.097 (3)*
H62	1.1266	0.4193	0.0812	0.097 (3)*
H63	1.2531	0.4175	0.2491	0.097 (3)*
C7	0.6373 (2)	0.29558 (11)	0.46148 (18)	0.0331 (3)
C8	0.5583 (2)	0.13178 (13)	0.4981 (2)	0.0457 (4)
H81	0.4432	0.1349	0.4281	0.097 (3)*
H82	0.5369	0.1442	0.6089	0.097 (3)*
H83	0.6114	0.0678	0.4909	0.097 (3)*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S	0.0442 (3)	0.0386 (3)	0.0618 (3)	0.00333 (17)	0.0247 (2)	0.00071 (18)
O	0.0395 (6)	0.0279 (6)	0.0560 (7)	−0.0006 (4)	0.0165 (5)	0.0023 (5)
N	0.0409 (7)	0.0272 (7)	0.0481 (8)	0.0021 (5)	0.0153 (6)	−0.0026 (6)
C1	0.0348 (7)	0.0260 (7)	0.0367 (7)	0.0016 (6)	0.0062 (6)	−0.0008 (5)
C2	0.0349 (7)	0.0299 (7)	0.0340 (7)	0.0018 (6)	0.0047 (6)	−0.0011 (6)
C3	0.0380 (8)	0.0330 (8)	0.0403 (8)	−0.0015 (6)	0.0093 (6)	0.0009 (6)
C4	0.0453 (9)	0.0274 (7)	0.0516 (9)	−0.0024 (6)	0.0140 (7)	0.0018 (6)
C5	0.0396 (8)	0.0332 (8)	0.0500 (9)	0.0067 (6)	0.0104 (7)	−0.0020 (7)
C6	0.0451 (9)	0.0466 (10)	0.0563 (10)	−0.0021 (8)	0.0202 (8)	0.0057 (8)
C7	0.0342 (7)	0.0312 (7)	0.0341 (7)	0.0008 (6)	0.0043 (6)	−0.0005 (6)
C8	0.0456 (9)	0.0325 (8)	0.0618 (11)	−0.0076 (7)	0.0176 (8)	0.0040 (8)

Geometric parameters (Å, °)

S—C7	1.6498 (16)	C3—C6	1.499 (2)
O—C7	1.3403 (19)	C4—H4	0.9500
O—C8	1.441 (2)	C5—H51	0.9800
N—C4	1.346 (2)	C5—H52	0.9800
N—C1	1.381 (2)	C5—H53	0.9800
N—H7	0.84 (2)	C6—H61	0.9800
C1—C2	1.399 (2)	C6—H62	0.9800
C1—C7	1.432 (2)	C6—H63	0.9800
C2—C3	1.413 (2)	C8—H81	0.9800
C2—C5	1.497 (2)	C8—H82	0.9800
C3—C4	1.385 (2)	C8—H83	0.9800
C7—O—C8	118.20 (13)	C2—C5—H53	109.5
C4—N—C1	109.80 (14)	H51—C5—H53	109.5
C4—N—H7	123.6 (14)	H52—C5—H53	109.5
C1—N—H7	126.6 (14)	C3—C6—H61	109.5
N—C1—C2	107.02 (13)	C3—C6—H62	109.5
N—C1—C7	119.71 (14)	H61—C6—H62	109.5
C2—C1—C7	133.22 (14)	C3—C6—H63	109.5
C1—C2—C3	107.27 (13)	H61—C6—H63	109.5
C1—C2—C5	127.87 (14)	H62—C6—H63	109.5

C3—C2—C5	124.85 (15)	O—C7—C1	111.52 (13)
C4—C3—C2	106.88 (14)	O—C7—S	124.00 (12)
C4—C3—C6	125.78 (15)	C1—C7—S	124.48 (12)
C2—C3—C6	127.34 (15)	O—C8—H81	109.5
N—C4—C3	109.02 (14)	O—C8—H82	109.5
N—C4—H4	125.5	H81—C8—H82	109.5
C3—C4—H4	125.5	O—C8—H83	109.5
C2—C5—H51	109.5	H81—C8—H83	109.5
C2—C5—H52	109.5	H82—C8—H83	109.5
H51—C5—H52	109.5		

Hydrogen-bond geometry (Å, °)

D—H⋯*A*	*D*—H	H⋯*A*	*D*⋯*A*	*D*—H⋯*A*
N—H7⋯S[i]	0.84 (2)	2.69 (2)	3.3622 (15)	138.7 (18)

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

Fig. 1

Fig. 2

Fig. 3

Fig. 4