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ISSN 2414-3146

1,3-Bis(1-methyl-5-thioxo-1,2,4-triazolin-4-yl)urea

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Received 2 June 2016
Accepted 17 June 2016

Edited by A. J. Lough, University of Toronto, Canada

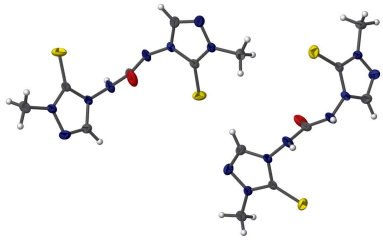
Keywords: crystal structure; carbohydrazide; N—H···O hydrogen bonds; triazole; urea.

CCDC reference: 1486393

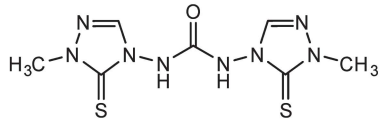
Structural data: full structural data are available from iucrdata.iucr.org

The title compound, $C_7H_{10}N_8OS_2$, was obtained by acylation of 4-amino-1-methyl-1,2,4-triazoline-5-thione with triphosgene. The asymmetric unit contains two half molecules. The full molecules are generated by twofold rotation axes. In the crystal, the molecules associate through bifurcated $(N—H)_2\cdots O$ hydrogen bonds into chains extending in the *b*-axis direction.

3D view



Chemical scheme



Structure description

The asymmetric unit contains two half-molecules. The fragments are completed by twofold rotation axes through the C4═O1 and C8═O2 carbonyl bonds. The molecular structures of the two independent molecules of the title compound are shown in Fig. 1. The amidic NH atoms adopt an *anti* relationship to the carbonyl group. Each molecule donates two N—H hydrogen bonds to the O atom of the O═C carbonyl group of one neighbouring molecule, forming infinite chains (Fig. 2). The intermolecular linkage is described as $R_2^1(6)$ in graph-set notation (Etter, 1990), denoting a hydrogen-bonded ring motif consisting of six atoms with two donors and one acceptor. The chains extend in opposite directions along the *b* axis. The hydrogen-bond parameters are summarized in Table 1, and the crystal packing is shown in Fig. 2.

Chains formed by bifurcated N—H···O hydrogen bonds are a typical pattern in the crystal structures of symmetrically *N*,*N*′-disubstituted ureas (Custelcean, 2008). The more closely related 1,5-bis(benzylidene)carbohydrazides (Kolb *et al.*, 1994; Li *et al.*, 2009; Rubčić *et al.*, 2014) exhibit a similar architecture.

Synthesis and crystallization

A solution of 4-amino-1-methyl-1,2,4-triazoline-5-thione (Laus *et al.*, 2014) (70 mg, 0.54 mmol) and triphosgene (74 mg, 0.25 mmol) in CH_2Cl_2 (2 ml) was stirred at room

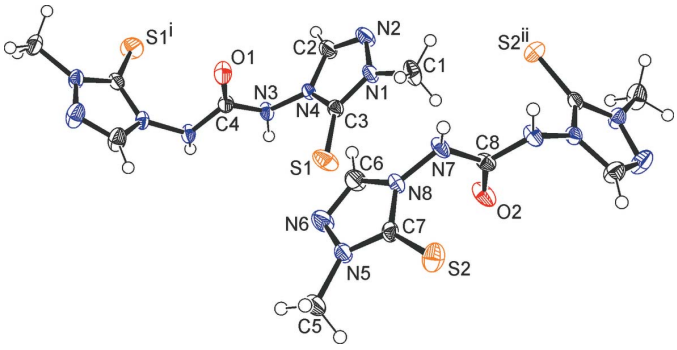


Figure 1
The two independent molecules of the title compound, showing the atom labels and 50% probability displacement ellipsoids for non-H atoms. [Symmetry codes: (i) $-\frac{1}{2}-x, y, \frac{1}{2}-z$; (ii) $\frac{1}{2}-x, y, \frac{1}{2}-z$.]

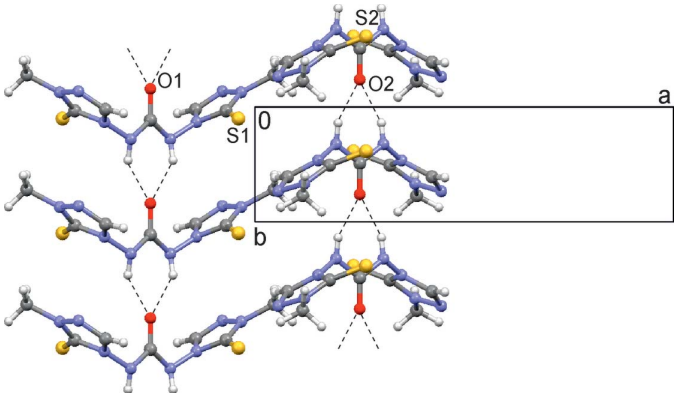


Figure 2
The crystal packing of the title compound, viewed along the *c* axis, showing the N—H···O hydrogen bonds as dashed lines (see Table 1).

temperature overnight. The solvent was removed under reduced pressure, and the residue was dissolved in hot MeOH (1 ml). On cooling to 253 K the product was obtained as colourless crystals (47 mg, 61%), m.p. 497–498 K.

^{1}H NMR (300 MHz, DMSO-d_6): δ 3.68 (*s*, 3H), 8.76 (*s*, 1H), 11.0 (*br s*, 2H) p.p.m. ^{13}C NMR (75 MHz, DMSO-d_6): δ 36.7 (2 C), 141.7 (2 C), 155.3, 166.2 (2 C) p.p.m. IR: ν 3264, 3223, 3114, 3040, 2940, 1689, 1532, 1461, 1380, 1341, 1238, 1202, 1159, 962, 878, 836, 766, 735, 623 cm^{-1}.

Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2.

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

D—H···A	D—H	H···A	D···A	D—H···A
N3—H3···O1^{iii}	0.84 (2)	2.02 (2)	2.753 (2)	145 (2)
N7—H7···O2^{iv}	0.83 (2)	2.02 (2)	2.755 (2)	147 (2)

Symmetry codes: (iii) $x, y+1, z$; (iv) $x, y-1, z$.

Table 2
Experimental details.

Crystal data	
Chemical formula	$C_7H_{10}N_8OS_2$
M_r	286.35
Crystal system, space group	Monoclinic, *P*2/*n*
Temperature (K)	173
a, *b*, *c* (Å)	16.5100 (8), 4.4590 (2), 17.5229 (8)
β (°)	98.108 (5)
V (Å^3)	1277.11 (10)
Z	4
Radiation type	Mo $K\alpha$
μ (mm^{-1})	0.42
Crystal size (mm)	0.32 × 0.16 × 0.16
Data collection	
Diffractometer	Oxford Diffraction Xcalibur Ruby Gemini ultra
Absorption correction	Multi-scan (*CrysAlis PRO*; Oxford Diffraction, 2010)
T_{min}, T_{max}	0.906, 1
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	7200, 2347, 1999
R_{int}	0.027
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.602
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.033, 0.078, 1.04
No. of reflections	2347
No. of parameters	175
No. of restraints	2
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.31, −0.29

Computer programs: *CrysAlis PRO* (Oxford Diffraction, 2010), *SIR2002* (Burla *et al.*, 2003), *SHELXL97* (Sheldrick, 2008), *ORTEP-3 for Windows* (Farrugia, 2012) and *Mercury* (Macrae *et al.*, 2006).

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full crystallographic data

IUCrData (2016). **1**, x160992 [doi:10.1107/S2414314616009925]

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Crystal data

$C_7H_{10}N_8OS_2$
M_r = 286.35
Monoclinic, $P2/n$
Hall symbol: -P 2yac
a = 16.5100 (8) Å
b = 4.4590 (2) Å
c = 17.5229 (8) Å
β = 98.108 (5)°
V = 1277.11 (10) Å^3
Z = 4
$F(000)$ = 592
D_x = 1.489 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 3315 reflections
θ = 3.2–28.7°
μ = 0.42 mm^{-1}
T = 173 K
Fragment, colourless
0.32 × 0.16 × 0.16 mm

Data collection

Oxford Diffraction Xcalibur Ruby Gemini ultra diffractometer
Graphite monochromator
Detector resolution: 10.3575 pixels mm^{-1}
ω scans
Absorption correction: multi-scan (CrysAlis PRO; Oxford Diffraction, 2010)
T_{min} = 0.906, T_{max} = 1
7200 measured reflections
2347 independent reflections
1999 reflections with $I > 2\sigma(I)$
R_{int} = 0.027
θ_{max} = 25.4°, θ_{min} = 3.2°
h = −19→19
k = −5→4
l = −21→17

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.033
$wR(F^2)$ = 0.078
S = 1.04
2347 reflections
175 parameters
2 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0258P)^2 + 0.834P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.31 e Å^{-3}
$\Delta\rho_{min}$ = −0.29 e Å^{-3}

Special details

Experimental. CrysAlisPro, Oxford Diffraction Ltd., Version 1.171.34.44 (release 25-10-2010 CrysAlis171 .NET) (compiled Oct 25 2010,18:11:34) Empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm.

Geometry. All s.u.'s (except the s.u. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell s.u.'s are taken into account individually in the estimation of s.u.'s in distances, angles and torsion angles; correlations between s.u.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell s.u.'s is used for estimating s.u.'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 $F^2 > 2\sigma(F^2)$ 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 (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
S2	0.26495 (3)	−0.61481 (13)	0.04670 (3)	0.03468 (16)
S1	−0.03987 (4)	0.10034 (14)	0.23836 (3)	0.03999 (17)
N4	−0.13996 (8)	0.1301 (3)	0.34860 (8)	0.0202 (3)
N8	0.15021 (8)	−0.5348 (3)	0.14215 (8)	0.0201 (3)
N2	−0.07827 (10)	−0.1375 (4)	0.44368 (9)	0.0351 (4)
N5	0.11782 (9)	−0.3325 (4)	0.03299 (8)	0.0246 (4)
N7	0.19327 (10)	−0.6770 (4)	0.20465 (9)	0.0240 (4)
N3	−0.20273 (9)	0.2794 (3)	0.30443 (9)	0.0232 (4)
O1	−0.25	−0.1591 (4)	0.25	0.0347 (5)
C3	−0.06949 (11)	0.0319 (4)	0.32286 (10)	0.0213 (4)
O2	0.25	−0.2394 (4)	0.25	0.0346 (5)
N6	0.05551 (9)	−0.2662 (4)	0.07491 (9)	0.0336 (4)
N1	−0.03351 (9)	−0.1290 (4)	0.38286 (8)	0.0245 (4)
C7	0.17800 (10)	−0.4933 (4)	0.07239 (10)	0.0201 (4)
C6	0.07744 (11)	−0.3923 (5)	0.14090 (11)	0.0292 (5)
H6	0.0468	−0.3861	0.1829	0.035*
C4	−0.25	0.1126 (6)	0.25	0.0220 (6)
C2	−0.14226 (11)	0.0200 (5)	0.42055 (11)	0.0319 (5)
H2	−0.1855	0.0549	0.4499	0.038*
C1	0.04523 (12)	−0.2800 (5)	0.38851 (11)	0.0342 (5)
H1A	0.0463	−0.4082	0.3432	0.051*
H1B	0.0535	−0.4032	0.4353	0.051*
H1C	0.0889	−0.1302	0.3908	0.051*
C8	0.25	−0.5107 (6)	0.25	0.0209 (5)
C5	0.11379 (12)	−0.2272 (5)	−0.04599 (11)	0.0349 (5)
H5A	0.1586	−0.0862	−0.0495	0.052*
H5B	0.0613	−0.1263	−0.0616	0.052*
H5C	0.1187	−0.3983	−0.0801	0.052*
H7	0.1984 (11)	−0.861 (3)	0.2012 (11)	0.022 (5)*
H3	−0.1963 (11)	0.464 (4)	0.2968 (11)	0.026 (5)*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S2	0.0233 (3)	0.0416 (3)	0.0397 (3)	0.0065 (2)	0.0063 (2)	−0.0075 (2)
S1	0.0508 (3)	0.0496 (4)	0.0214 (3)	0.0104 (3)	0.0119 (2)	0.0080 (2)
N4	0.0187 (7)	0.0204 (8)	0.0198 (7)	0.0013 (6)	−0.0028 (6)	0.0040 (6)

N8	0.0218 (8)	0.0207 (8)	0.0164 (7)	0.0031 (6)	−0.0023 (6)	0.0015 (6)
N2	0.0277 (9)	0.0534 (12)	0.0251 (9)	0.0094 (8)	0.0065 (7)	0.0170 (8)
N5	0.0197 (8)	0.0357 (9)	0.0184 (8)	0.0037 (7)	0.0024 (6)	0.0054 (7)
N7	0.0334 (9)	0.0130 (8)	0.0219 (8)	0.0007 (7)	−0.0084 (7)	0.0019 (6)
N3	0.0246 (8)	0.0122 (8)	0.0292 (8)	0.0014 (6)	−0.0091 (7)	0.0015 (7)
O1	0.0340 (11)	0.0115 (10)	0.0524 (13)	0	−0.0156 (10)	0
C3	0.0236 (9)	0.0203 (9)	0.0188 (9)	−0.0019 (7)	−0.0015 (7)	−0.0011 (7)
O2	0.0548 (13)	0.0124 (10)	0.0309 (10)	0	−0.0138 (9)	0
N6	0.0262 (9)	0.0472 (11)	0.0288 (9)	0.0132 (8)	0.0085 (7)	0.0122 (8)
N1	0.0215 (8)	0.0328 (9)	0.0184 (8)	0.0049 (7)	0.0003 (6)	0.0053 (7)
C7	0.0197 (9)	0.0205 (9)	0.0188 (9)	−0.0025 (7)	−0.0022 (7)	−0.0035 (7)
C6	0.0266 (10)	0.0367 (12)	0.0252 (10)	0.0074 (9)	0.0066 (8)	0.0050 (9)
C4	0.0211 (13)	0.0163 (14)	0.0271 (14)	0	−0.0020 (11)	0
C2	0.0235 (10)	0.0465 (13)	0.0260 (10)	0.0040 (9)	0.0048 (8)	0.0115 (9)
C1	0.0275 (10)	0.0451 (13)	0.0285 (10)	0.0151 (9)	−0.0013 (9)	0.0010 (9)
C8	0.0294 (14)	0.0149 (13)	0.0175 (12)	0	0.0002 (11)	0
C5	0.0289 (10)	0.0543 (14)	0.0209 (10)	0.0006 (10)	0.0018 (8)	0.0121 (9)

Geometric parameters (Å, º)

S2—C7	1.6551 (18)	N3—H3	0.842 (15)
S1—C3	1.6520 (18)	O1—C4	1.211 (3)
N4—C2	1.359 (2)	C3—N1	1.340 (2)
N4—N3	1.3749 (19)	O2—C8	1.210 (3)
N4—C3	1.377 (2)	N6—C6	1.291 (2)
N8—C6	1.357 (2)	N1—C1	1.455 (2)
N8—N7	1.3737 (19)	C6—H6	0.95
N8—C7	1.377 (2)	C4—N3^{i}	1.365 (2)
N2—C2	1.286 (2)	C2—H2	0.95
N2—N1	1.380 (2)	C1—H1A	0.98
N5—C7	1.336 (2)	C1—H1B	0.98
N5—N6	1.378 (2)	C1—H1C	0.98
N5—C5	1.454 (2)	C8—N7^{ii}	1.360 (2)
N7—C8	1.360 (2)	C5—H5A	0.98
N7—H7	0.829 (15)	C5—H5B	0.98
N3—C4	1.365 (2)	C5—H5C	0.98
C2—N4—N3	125.45 (16)	N8—C7—S2	127.42 (13)
C2—N4—C3	108.93 (14)	N6—C6—N8	110.76 (17)
N3—N4—C3	125.05 (15)	N6—C6—H6	124.6
C6—N8—N7	125.91 (15)	N8—C6—H6	124.6
C6—N8—C7	109.13 (14)	O1—C4—N3	123.04 (11)
N7—N8—C7	124.75 (15)	O1—C4—N3^{i}	123.04 (11)
C2—N2—N1	104.32 (15)	N3—C4—N3^{i}	113.9 (2)
C7—N5—N6	113.36 (14)	N2—C2—N4	111.14 (17)
C7—N5—C5	126.59 (16)	N2—C2—H2	124.4
N6—N5—C5	120.05 (14)	N4—C2—H2	124.4
C8—N7—N8	116.79 (16)	N1—C1—H1A	109.5

C8—N7—H7	120.9 (13)	N1—C1—H1B	109.5
N8—N7—H7	116.5 (13)	H1A—C1—H1B	109.5
C4—N3—N4	116.15 (15)	N1—C1—H1C	109.5
C4—N3—H3	119.6 (13)	H1A—C1—H1C	109.5
N4—N3—H3	117.4 (13)	H1B—C1—H1C	109.5
N1—C3—N4	102.41 (15)	O2—C8—N7	123.05 (11)
N1—C3—S1	130.35 (14)	O2—C8—N7^{ii}	123.05 (11)
N4—C3—S1	127.25 (13)	N7—C8—N7^{ii}	113.9 (2)
C6—N6—N5	104.35 (15)	N5—C5—H5A	109.5
C3—N1—N2	113.19 (14)	N5—C5—H5B	109.5
C3—N1—C1	126.44 (16)	H5A—C5—H5B	109.5
N2—N1—C1	120.36 (14)	N5—C5—H5C	109.5
N5—C7—N8	102.38 (14)	H5A—C5—H5C	109.5
N5—C7—S2	130.21 (14)	H5B—C5—H5C	109.5
C6—N8—N7—C8	−92.0 (2)	C5—N5—C7—N8	−178.91 (18)
C7—N8—N7—C8	82.2 (2)	N6—N5—C7—S2	−178.16 (15)
C2—N4—N3—C4	−98.5 (2)	C5—N5—C7—S2	1.4 (3)
C3—N4—N3—C4	71.8 (2)	C6—N8—C7—N5	−1.55 (19)
C2—N4—C3—N1	−0.91 (19)	N7—N8—C7—N5	−176.56 (15)
N3—N4—C3—N1	−172.58 (15)	C6—N8—C7—S2	178.12 (14)
C2—N4—C3—S1	178.80 (15)	N7—N8—C7—S2	3.1 (3)
N3—N4—C3—S1	7.1 (3)	N5—N6—C6—N8	−0.2 (2)
C7—N5—N6—C6	−0.9 (2)	N7—N8—C6—N6	176.08 (17)
C5—N5—N6—C6	179.50 (18)	C7—N8—C6—N6	1.1 (2)
N4—C3—N1—N2	0.6 (2)	N4—N3—C4—O1	15.64 (17)
S1—C3—N1—N2	−179.12 (15)	N4—N3—C4—N3^{i}	−164.36 (17)
N4—C3—N1—C1	−178.04 (17)	N1—N2—C2—N4	−0.6 (2)
S1—C3—N1—C1	2.3 (3)	N3—N4—C2—N2	172.63 (17)
C2—N2—N1—C3	0.0 (2)	C3—N4—C2—N2	1.0 (2)
C2—N2—N1—C1	178.71 (18)	N8—N7—C8—O2	19.06 (18)
N6—N5—C7—N8	1.5 (2)	N8—N7—C8—N7^{ii}	−160.94 (18)

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

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N3—H3···O1^{iii}	0.84 (2)	2.02 (2)	2.753 (2)	145 (2)
N7—H7···O2^{iv}	0.83 (2)	2.02 (2)	2.755 (2)	147 (2)

Symmetry codes: (iii) *x*, *y*+1, *z*; (iv) *x*, *y*−1, *z*.