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1,1′-(Ethane-1,2-diyl)bis[3-(4-chlorobenzoyl)thiourea]

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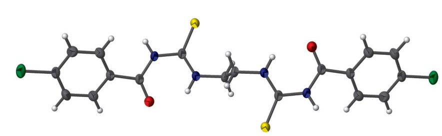
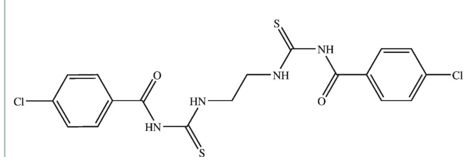
Structural data: full structural data are available from iucrdata.iucr.org

The title compound, $C_{18}H_{16}Cl_2N_4O_2S_2$, consists of two benzoylthioureido groups connected by an ethylene group. The asymmetric unit consists of one half of the molecule which lies about an inversion center. Both thiourea moieties maintain their *trans* geometry. The structure is stabilized by intermolecular N—H⋯S hydrogen bonds that form chains along the *b*-axis direction.

3D view



Chemical scheme



Structure description

Multipodal thiourea compounds are expected to be useful for molecular recognition studies and as ionophores for sensor development due to the nucleophilic nature of the sulfur atoms. In addition, the biological properties of thiourea are well known (Korkmaz *et al.*, 2015). 1,1′-(Ethane-1,2-diyl)bis(3-phenylthiourea) is one of the few reported bis-thiourea structures with an ethylene group as linker (Pansuriya *et al.*, 2011). The present compound is similar except that it is a benzoyl rather than a phenylthiourea derivative. The asymmetric unit consists of one half of the molecule as the molecule lies about a center of inversion located at the midpoint of the C9—C9*A* bond (Fig. 1). Both thiourea moieties adopt a *trans* geometry and the thiono groups are also in a *trans* orientation with respect to the chlorobenzoyl group. The thiourea fragments S1/N1/N2/C7/C8 are planar with a maximum deviation from the least-squares plane of 0.008 (1) Å for the N1 atom. The dihedral angle between this plane and that of the benzene ring is 34.48 (8)°, which is considerably smaller than that found in 1,1′-(ethane-1,2-diyl)bis(3-phenylthiourea), 52.9 (4)°. Other bond lengths and angles are comparable to those in the analog and lie in normal ranges. As with most carbonoylthiourea derivatives, the molecule forms intramolecular N2—H2*A*⋯O1 hydrogen bonds between the carbonyl oxygen and the thioamide hydrogen atoms, to form *S*(6) rings.

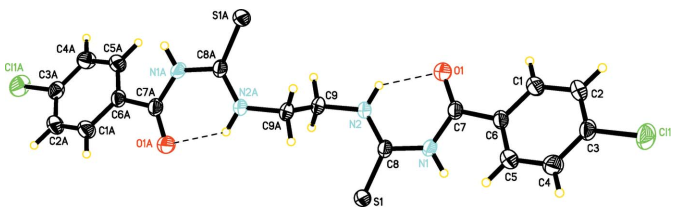


Figure 1
The molecular structure with displacement ellipsoids drawn at the 50% probability level. The dashed lines indicate intramolecular hydrogen bonds.

In the crystal packing, molecules are linked by inversion-related intermolecular N1—H1*A*···S1 hydrogen bonds (Table 1), forming chains along the *b*-axis direction (Fig. 2).

Synthesis and crystallization

An acetonitrile solution (30 ml) of ethylenediamine (0.30 g, 0.005 mol) was added dropwise into a two-necked round-bottomed flask containing 4-chlorobenzoylisothiocyanate (1.96 g, 0.01 mol). The mixture was refluxed for about 4 h, filtered into a beaker and left for the solvent to evaporate at room temperature. The resulting yellow precipitate was washed with cold ethanol. Crystals suitable for X-ray study were obtained by recrystallization from DMSO.

Refinement

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

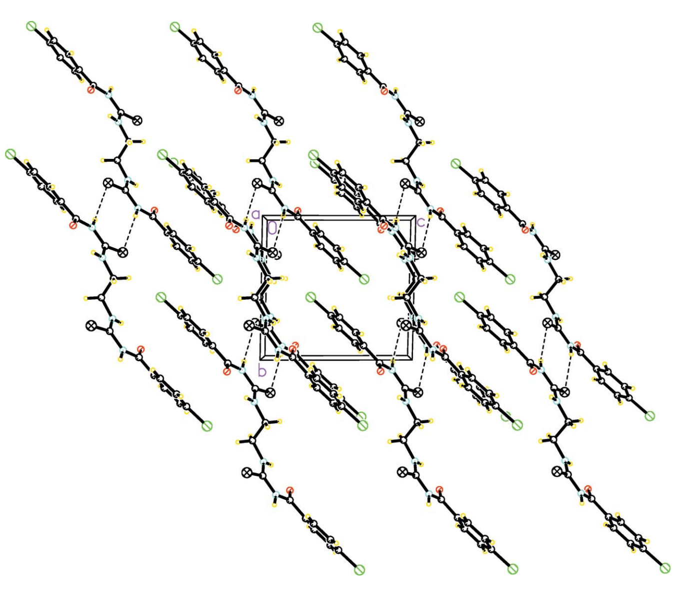


Figure 2
The crystal packing of the title compound viewed along the *a* axis. The dashed lines indicate hydrogen bonds.

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

D—H···A	D—H	H···A	D···A	D—H···A
N2—H2*A*···O1	0.87 (2)	2.01 (3)	2.670 (2)	133 (2)
N1—H1*A*···S1^{i}	0.86 (1)	2.73 (2)	3.5203 (14)	153 (1)

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

Table 2
Experimental details.

Crystal data	
Chemical formula	$C_{18}H_{16}Cl_2N_4O_2S_2$
M_r	455.37
Crystal system, space group	Triclinic, $P\overline{1}$
Temperature (K)	300
a, b, c (Å)	6.0099 (3), 8.7905 (4), 9.2603 (4)
α, β, γ (°)	91.030 (2), 91.835 (2), 94.878 (2)
V (Å^3)	487.09 (4)
Z	1
Radiation type	Mo $K\alpha$
μ (mm^{-1})	0.57
Crystal size (mm)	0.50 × 0.47 × 0.10
Data collection	
Diffractometer	Bruker SMART APEX CCD area-detector diffractometer
Absorption correction	Multi-scan (*SADABS*; Bruker, 2000)
T_{min}, T_{max}	0.763, 0.945
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	20610, 2421, 1985
R_{int}	0.054
$(\sin \theta/\lambda)_{max}$ (Å^{-1})	0.672
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.036, 0.094, 1.06
No. of reflections	2421
No. of parameters	135
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})	0.22, −0.40

Computer programs: *SMART* and *SAINT* (Bruker, 2000), *SHELXS97*, *SHELXL97* and *SHELXTL* (Sheldrick, 2008) and *PLATON* (Spek, 2009).

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full crystallographic data

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1,1′-(Ethane-1,2-diyl)bis[3-(4-chlorobenzoyl)thiourea]

Crystal data

$C_{18}H_{16}Cl_2N_4O_2S_2$
$M_r = 455.37$
Triclinic, $P\bar{1}$
Hall symbol: -P 1
$a = 6.0099$ (3) Å
$b = 8.7905$ (4) Å
$c = 9.2603$ (4) Å
$\alpha = 91.030$ (2)°
$\beta = 91.835$ (2)°
$\gamma = 94.878$ (2)°
$V = 487.09$ (4) Å^3
$Z = 1$
$F(000) = 234$
$D_x = 1.552$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 20610 reflections
$\theta = 3.1$–28.5°
$\mu = 0.57$ mm^{-1}
$T = 300$ K
Block, colourless
0.50 × 0.47 × 0.10 mm

Data collection

Bruker SMART APEX CCD area-detector diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
Detector resolution: 83.66 pixels mm^{-1}
ω scans
Absorption correction: multi-scan (SADABS; Bruker, 2000)
$T_{min} = 0.763$, $T_{max} = 0.945$
20610 measured reflections
2421 independent reflections
1985 reflections with $I > 2\sigma(I)$
$R_{int} = 0.054$
$\theta_{max} = 28.5°$, $\theta_{min} = 3.2°$
$h = -8 \rightarrow 8$
$k = -11 \rightarrow 11$
$l = -12 \rightarrow 12$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.036$
$wR(F^2) = 0.094$
$S = 1.06$
2421 reflections
135 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
$w = 1/[\sigma^2(F_o^2) + (0.0389P)^2 + 0.2974P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.22$ e Å^{-3}
$\Delta\rho_{min} = -0.40$ e Å^{-3}

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds 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 $F^2 > 2\text{sigma}(F^2)$ 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}
Cl1	0.35967 (9)	1.43588 (6)	0.67959 (5)	0.04843 (16)
S1	0.41800 (7)	0.75184 (5)	−0.05845 (5)	0.03377 (14)
O1	−0.1332 (2)	0.92654 (15)	0.20898 (15)	0.0379 (3)
N1	0.2191 (2)	0.92314 (16)	0.12526 (16)	0.0310 (3)
H1A	0.342 (2)	0.981 (2)	0.120 (2)	0.035 (5)*
N2	0.0029 (2)	0.71056 (16)	0.03437 (17)	0.0306 (3)
H2A	−0.107 (3)	0.743 (3)	0.081 (3)	0.059 (8)*
C1	−0.0034 (3)	1.1925 (2)	0.3763 (2)	0.0350 (4)
H1	−0.1497	1.1852	0.3394	0.042*
C2	0.0614 (3)	1.2974 (2)	0.4854 (2)	0.0377 (4)
H2	−0.0401	1.3614	0.5215	0.045*
C3	0.2780 (3)	1.3064 (2)	0.54035 (18)	0.0315 (4)
C4	0.4312 (3)	1.2145 (2)	0.4867 (2)	0.0353 (4)
H4	0.5772	1.2221	0.5243	0.042*
C5	0.3664 (3)	1.1105 (2)	0.37613 (19)	0.0320 (4)
H5	0.4696	1.0488	0.3386	0.038*
C6	0.1481 (3)	1.09795 (18)	0.32110 (17)	0.0264 (3)
C7	0.0619 (3)	0.97689 (18)	0.21382 (18)	0.0272 (3)
C8	0.1979 (3)	0.79277 (18)	0.03623 (18)	0.0263 (3)
C9	−0.0421 (3)	0.56512 (18)	−0.0434 (2)	0.0311 (4)
H9A	0.0307	0.5703	−0.1354	0.037*
H9B	−0.2016	0.5455	−0.0626	0.037*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cl1	0.0560 (3)	0.0468 (3)	0.0394 (3)	−0.0113 (2)	0.0062 (2)	−0.0203 (2)
S1	0.0291 (2)	0.0325 (2)	0.0389 (3)	−0.00209 (17)	0.00894 (17)	−0.01205 (18)
O1	0.0314 (7)	0.0346 (7)	0.0465 (8)	−0.0026 (5)	0.0073 (5)	−0.0130 (6)
N1	0.0312 (8)	0.0248 (7)	0.0352 (8)	−0.0084 (6)	0.0113 (6)	−0.0112 (6)
N2	0.0280 (7)	0.0213 (7)	0.0419 (8)	−0.0017 (5)	0.0087 (6)	−0.0104 (6)
C1	0.0296 (9)	0.0348 (9)	0.0406 (10)	0.0045 (7)	0.0017 (7)	−0.0106 (8)
C2	0.0380 (10)	0.0327 (9)	0.0426 (10)	0.0054 (8)	0.0077 (8)	−0.0136 (8)
C3	0.0392 (9)	0.0271 (8)	0.0270 (8)	−0.0044 (7)	0.0065 (7)	−0.0070 (6)
C4	0.0309 (9)	0.0407 (10)	0.0334 (9)	0.0005 (7)	0.0003 (7)	−0.0059 (7)
C5	0.0322 (9)	0.0318 (9)	0.0324 (9)	0.0048 (7)	0.0048 (7)	−0.0055 (7)

C6	0.0330 (9)	0.0210 (7)	0.0250 (8)	0.0004 (6)	0.0056 (6)	−0.0027 (6)
C7	0.0329 (9)	0.0209 (7)	0.0275 (8)	−0.0002 (6)	0.0051 (6)	−0.0029 (6)
C8	0.0302 (8)	0.0199 (7)	0.0285 (8)	−0.0006 (6)	0.0034 (6)	−0.0035 (6)
C9	0.0293 (8)	0.0223 (8)	0.0403 (10)	−0.0034 (6)	0.0013 (7)	−0.0111 (7)

Geometric parameters (Å, º)

Cl1—C3	1.7354 (17)	C2—C3	1.378 (3)
S1—C8	1.6709 (17)	C2—H2	0.9300
O1—C7	1.217 (2)	C3—C4	1.374 (3)
N1—C7	1.378 (2)	C4—C5	1.384 (3)
N1—C8	1.394 (2)	C4—H4	0.9300
N1—H1A	0.862 (9)	C5—C6	1.386 (3)
N2—C8	1.323 (2)	C5—H5	0.9300
N2—C9	1.456 (2)	C6—C7	1.491 (2)
N2—H2A	0.865 (10)	C9—C9^{i}	1.522 (4)
C1—C2	1.380 (3)	C9—H9A	0.9700
C1—C6	1.387 (2)	C9—H9B	0.9700
C1—H1	0.9300		
C7—N1—C8	127.96 (14)	C4—C5—C6	120.32 (16)
C7—N1—H1A	115.7 (14)	C4—C5—H5	119.8
C8—N1—H1A	116.2 (14)	C6—C5—H5	119.8
C8—N2—C9	123.80 (14)	C5—C6—C1	119.30 (16)
C8—N2—H2A	119.6 (18)	C5—C6—C7	122.74 (15)
C9—N2—H2A	116.6 (18)	C1—C6—C7	117.72 (16)
C2—C1—C6	120.52 (17)	O1—C7—N1	122.85 (15)
C2—C1—H1	119.7	O1—C7—C6	121.59 (15)
C6—C1—H1	119.7	N1—C7—C6	115.52 (14)
C3—C2—C1	119.29 (17)	N2—C8—N1	116.65 (14)
C3—C2—H2	120.4	N2—C8—S1	125.18 (12)
C1—C2—H2	120.4	N1—C8—S1	118.17 (12)
C4—C3—C2	121.17 (16)	N2—C9—C9^{i}	111.15 (18)
C4—C3—Cl1	119.23 (14)	N2—C9—H9A	109.4
C2—C3—Cl1	119.60 (14)	C9^{i}—C9—H9A	109.4
C3—C4—C5	119.38 (17)	N2—C9—H9B	109.4
C3—C4—H4	120.3	C9^{i}—C9—H9B	109.4
C5—C4—H4	120.3	H9A—C9—H9B	108.0
C6—C1—C2—C3	−0.6 (3)	C8—N1—C7—C6	166.43 (17)
C1—C2—C3—C4	1.1 (3)	C5—C6—C7—O1	149.94 (18)
C1—C2—C3—Cl1	−179.00 (15)	C1—C6—C7—O1	−24.4 (3)
C2—C3—C4—C5	−0.4 (3)	C5—C6—C7—N1	−27.9 (2)
Cl1—C3—C4—C5	179.68 (14)	C1—C6—C7—N1	157.85 (16)
C3—C4—C5—C6	−0.7 (3)	C9—N2—C8—N1	−174.95 (16)
C4—C5—C6—C1	1.1 (3)	C9—N2—C8—S1	4.8 (3)
C4—C5—C6—C7	−173.06 (17)	C7—N1—C8—N2	0.8 (3)
C2—C1—C6—C5	−0.5 (3)	C7—N1—C8—S1	−178.87 (15)

C2—C1—C6—C7	174.04 (17)	C8—N2—C9—C9^{i}	81.7 (2)
C8—N1—C7—O1	−11.3 (3)		

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

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N2—H2*A*···O1	0.87 (2)	2.01 (3)	2.670 (2)	133 (2)
C9—H9*A*···S1	0.97	2.77	3.1017 (18)	101
N1—H1*A*···S1^{ii}	0.86 (1)	2.73 (2)	3.5203 (14)	153 (1)

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