organic compounds

1,1'-(Ethane-1,2-diyl)bis(3-phenylthiourea)

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The complete molecule of the title compound, $C_{16}H_{18}N_4S_2$, is generated by crystallographic inversion symmetry. The dihedral angle between the phenyl ring and the thiourea group is 52.9 (4)°. The crystal structure displays intermolecular N—H⋯S hydrogen bonding, which generates sheets in the *ab* plane.

Related literature

Bisthiourea and urea derivatives with alkane bridges can adopt two general shapes, bent (Pansuriya *et al.*, 2011*a*) or straight alkyl chains (Pansuriya *et al.*, 2011*b*; Koevoets *et al.*, 2005). For the synthesis see: Lee *et al.* (1985).
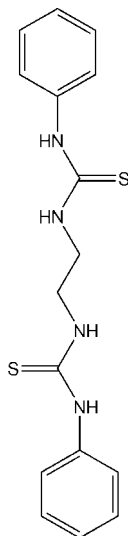
Experimental

Crystal data

$C_{16}H_{18}N_4S_2$	V = 1581.79 (10) Å^3
M_r = 330.46	Z = 4
Orthorhombic, $Pbca$	Mo $K\alpha$ radiation
a = 10.5823 (4) Å	μ = 0.34 mm^{-1}
b = 9.1053 (3) Å	T = 173 K
c = 16.4163 (6) Å	0.53 × 0.26 × 0.12 mm

Data collection

Bruker APEXII CCD diffractometer	1902 independent reflections
	1523 reflections with $I > 2\sigma(I)$
22438 measured reflections	R_{int} = 0.078

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.054	100 parameters
$wR(F^2)$ = 0.135	H-atom parameters constrained
S = 1.13	$\Delta\rho_{max}$ = 0.55 e Å^{-3}
1902 reflections	$\Delta\rho_{min}$ = −0.38 e Å^{-3}

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

D—H⋯A	D—H	H⋯A	D⋯A	D—H⋯A
N1—H1N⋯S1^i	0.88	2.57	3.379 (2)	153

Symmetry code: (i) $-x + \frac{3}{2}, y + \frac{1}{2}, z$.

Data collection: *APEX2* (Bruker, 2006); cell refinement: *SAINT* (Bruker, 2006); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *OLEX2* (Dolomanov *et al.*, 2009); software used to prepare material for publication: *SHELXTL* (Sheldrick, 2008).

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: PK2349).

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supporting information

1,1′-(Ethane-1,2-diyl)bis(3-phenylthiourea)

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S1. Comment

Thiourea and urea functionalized ligands play key roles in a wide range of catalytic reactions. Here we report the crystal structure of such a compound (Lee *et al.*, 1985) (Fig. 1). We recently reported a similar thiourea structure, where the molecules were bent (Pansuriya *et al.*, 2011*a*). Bisthiourea and urea derivatives with alkane bridges can adopt two general shapes, bent (Pansuriya *et al.*, 2011*a*) or straight alkyl chains (Pansuriya *et al.*, 2011*b*; Koevoets *et al.*, 2005). The spacer length between the two terminal thiourea or urea groups does not appear to influence the shape the bridging atoms take. The closest structure to the title compound 1,1′-(butane-1,4-diyl)bis(3-phenylthiourea) (Pansuriya *et al.*, 2011*a*) has also a *transoid* arrangement of the two thiourea groups. The asymmetric unit of the title compound is a half molecule and the complete molecule is generated by inversion symmetry (i): *1 - x, -y, 1 - z*. The structure shows intermolecular hydrogen bonding interactions between N1–H1···S1, 3.379 (2) Å, that creates sheets in the *ab* plane(Fig. 2). The dihedral angle between the phenyl ring and the thiourea group is 52.9 (4)°.

S2. Experimental

A solution of phenyl isothiocyanate (6.75 g, 50 mmol) in diethyl ether (15 ml) was added dropwise at 15 °C to a vigorously stirring solution of anhydrous ethane-1,2-diamine (6.01 g, 100 mmol) in isopropyl alcohol (100 ml) over a period of 30 min. The reaction mixture was stirred for 2 hrs at room temperature and quenched with water (200 ml). This reaction mixture was then maintained overnight at room temperature. Then the reaction mixture was acidified with conc. HCl up to pH 2.6. The solvents were evaporated under reduced pressure, the residue was suspended in hot water for 30 min. The resulting precipitate was filtered by vacuum. The product was washed with ice cold water and dried. The yield was 2.90 g (35%).

Crystals suitable for single-crystal X-ray diffraction analysis were grown in methanol: methylene chloride (1:2) at room temperature. M.p. = 462 K.

S3. Refinement

Hydrogen atoms were first located in the difference map then positioned geometrically and allowed to ride on their respective parent atoms with C—H distances of 0.95 Å (C_{ar}H), 0.99 Å (CH_2) and N—H distances of 0.88 Å. U_{iso}(H) values were set to 1.2 U_{eq} of the attached atom.
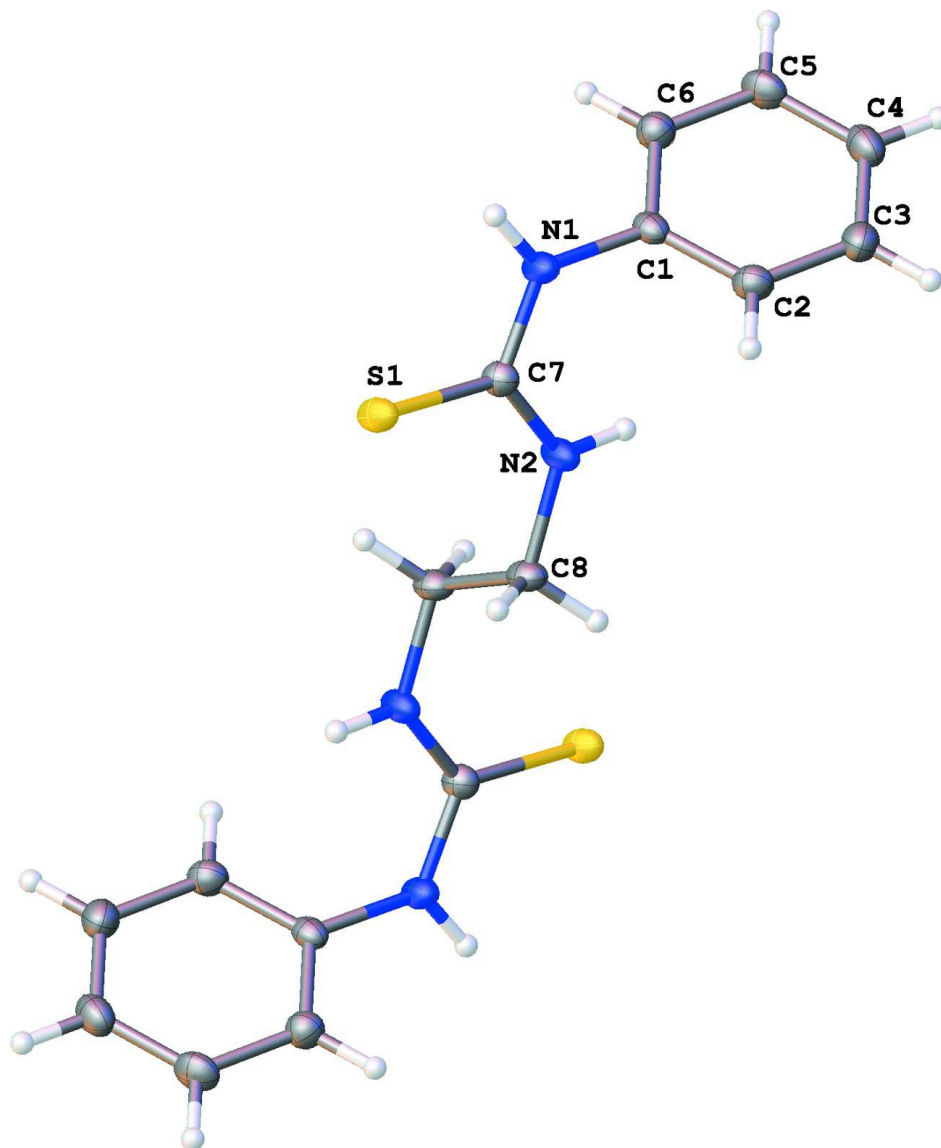
Figure 1

The molecular structure of the title compound. Displacement ellipsoids are drawn at the 40% probability level. The 1,1′-(ethane-1,2-diyl)bis(3-phenylthiourea) has inversion symmetry, so that unlabelled atoms are related by (1 - x, -y, 1 - z.
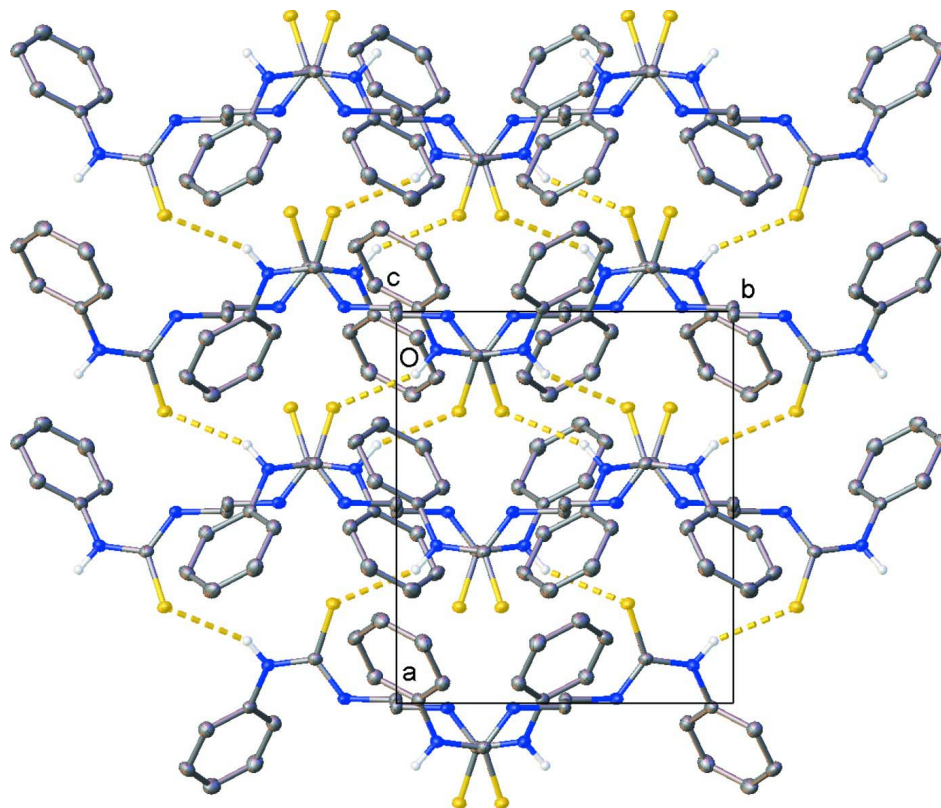
Figure 2
The crystal packing structure in the *ab* plane. All hydrogen atoms except those involved in hydrogen bonding interactions have been omitted for clarity.

1,1′-(Ethane-1,2-diyl)bis(3-phenylthiourea)

Crystal data

$C_{16}H_{18}N_4S_2$
$M_r = 330.46$
Orthorhombic, *Pbca*
Hall symbol: -P 2ac 2ab
$a = 10.5823$ (4) Å
$b = 9.1053$ (3) Å
$c = 16.4163$ (6) Å
$V = 1581.79$ (10) Å^3
$Z = 4$
$F(000) = 696$

$D_x = 1.388$ Mg m^{-3}
Melting point: 462 K
Mo *Kα* radiation, $\lambda = 0.71073$ Å
Cell parameters from 8682 reflections
$\theta = 2.5–28.3°$
$\mu = 0.34$ mm^{-1}
$T = 173$ K
Plate, colourless
$0.53 \times 0.26 \times 0.12$ mm

Data collection

Bruker APEXII CCD
  diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
φ and ω scans
22438 measured reflections
1902 independent reflections

1523 reflections with $I > 2\sigma(I)$
$R_{int} = 0.078$
$\theta_{max} = 28.0°$, $\theta_{min} = 2.5°$
$h = -13 \rightarrow 13$
$k = -12 \rightarrow 12$
$l = -21 \rightarrow 21$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	
$R[F^2 > 2\sigma(F^2)] = 0.054$	Hydrogen site location: inferred from neighbouring sites
$wR(F^2) = 0.135$	
$S = 1.13$	H-atom parameters constrained
1902 reflections	$w = 1/[\sigma^2(F_o^2) + (0.0373P)^2 + 3.3624P]$ where $P = (F_o^2 + 2F_c^2)/3$
100 parameters	
0 restraints	$(\Delta/\sigma)_{max} < 0.001$
Primary atom site location: structure-invariant direct methods	$\Delta\rho_{max} = 0.55$ e Å^{-3}
	$\Delta\rho_{min} = -0.38$ 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}
C1	0.4907 (2)	0.4345 (3)	0.35565 (15)	0.0229 (5)
C2	0.4488 (3)	0.3631 (3)	0.28604 (17)	0.0281 (6)
H2	0.4897	0.2763	0.2678	0.034*
C3	0.3463 (3)	0.4196 (3)	0.24308 (18)	0.0329 (6)
H3	0.3161	0.3700	0.1961	0.039*
C4	0.2885 (3)	0.5468 (3)	0.26835 (18)	0.0339 (6)
H4	0.2185	0.5848	0.2389	0.041*
C5	0.3321 (3)	0.6195 (3)	0.33647 (18)	0.0321 (6)
H5	0.2932	0.7086	0.3530	0.039*
C6	0.4330 (3)	0.5630 (3)	0.38118 (17)	0.0280 (6)
H6	0.4619	0.6121	0.4287	0.034*
C7	0.6127 (2)	0.2403 (3)	0.42665 (15)	0.0226 (5)
C8	0.5090 (3)	0.0019 (3)	0.45415 (16)	0.0263 (5)
H8A	0.5891	−0.0479	0.4398	0.032*
H8B	0.4389	−0.0520	0.4276	0.032*
N1	0.5975 (2)	0.3795 (2)	0.39925 (14)	0.0246 (5)
H1N	0.6591	0.4418	0.4092	0.030*
N2	0.5118 (2)	0.1523 (2)	0.42399 (14)	0.0258 (5)
H2N	0.4421	0.1877	0.4025	0.031*
S1	0.75428 (6)	0.18711 (7)	0.46353 (4)	0.0273 (2)

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0182 (11)	0.0206 (12)	0.0298 (12)	−0.0016 (9)	−0.0006 (10)	0.0067 (10)

C2	0.0263 (13)	0.0241 (13)	0.0338 (13)	0.0016 (11)	0.0008 (11)	0.0000 (11)
C3	0.0346 (15)	0.0306 (14)	0.0335 (14)	−0.0042 (12)	−0.0079 (12)	0.0026 (12)
C4	0.0268 (14)	0.0340 (15)	0.0407 (15)	−0.0005 (12)	−0.0072 (12)	0.0107 (12)
C5	0.0238 (13)	0.0281 (14)	0.0445 (16)	0.0071 (11)	0.0010 (12)	0.0039 (12)
C6	0.0265 (13)	0.0266 (13)	0.0309 (13)	0.0009 (11)	−0.0005 (10)	−0.0005 (11)
C7	0.0170 (11)	0.0230 (12)	0.0279 (12)	0.0013 (9)	0.0023 (10)	0.0006 (10)
C8	0.0229 (12)	0.0184 (11)	0.0376 (14)	−0.0016 (9)	−0.0004 (11)	0.0030 (10)
N1	0.0164 (10)	0.0196 (10)	0.0378 (12)	−0.0019 (8)	−0.0033 (9)	0.0024 (9)
N2	0.0152 (10)	0.0219 (11)	0.0403 (12)	−0.0003 (8)	−0.0024 (9)	0.0084 (9)
S1	0.0150 (3)	0.0218 (3)	0.0450 (4)	0.0017 (2)	−0.0026 (3)	0.0001 (3)

Geometric parameters (Å, º)

C1—C6	1.385 (4)	C6—H6	0.9500
C1—C2	1.387 (4)	C7—N2	1.336 (3)
C1—N1	1.428 (3)	C7—N1	1.354 (3)
C2—C3	1.393 (4)	C7—S1	1.687 (2)
C2—H2	0.9500	C8—N2	1.456 (3)
C3—C4	1.373 (4)	C8—C8^i	1.518 (5)
C3—H3	0.9500	C8—H8A	0.9900
C4—C5	1.379 (4)	C8—H8B	0.9900
C4—H4	0.9500	N1—H1N	0.8800
C5—C6	1.394 (4)	N2—H2N	0.8800
C5—H5	0.9500		
C6—C1—C2	120.3 (2)	C5—C6—H6	120.3
C6—C1—N1	119.6 (2)	N2—C7—N1	117.1 (2)
C2—C1—N1	120.1 (2)	N2—C7—S1	123.3 (2)
C1—C2—C3	119.5 (3)	N1—C7—S1	119.59 (19)
C1—C2—H2	120.2	N2—C8—C8^i	111.2 (3)
C3—C2—H2	120.2	N2—C8—H8A	109.4
C4—C3—C2	120.4 (3)	C8^i—C8—H8A	109.4
C4—C3—H3	119.8	N2—C8—H8B	109.4
C2—C3—H3	119.8	C8^i—C8—H8B	109.4
C3—C4—C5	120.0 (3)	H8A—C8—H8B	108.0
C3—C4—H4	120.0	C7—N1—C1	126.1 (2)
C5—C4—H4	120.0	C7—N1—H1N	117.0
C4—C5—C6	120.4 (3)	C1—N1—H1N	117.0
C4—C5—H5	119.8	C7—N2—C8	124.7 (2)
C6—C5—H5	119.8	C7—N2—H2N	117.6
C1—C6—C5	119.4 (3)	C8—N2—H2N	117.6
C1—C6—H6	120.3		
C6—C1—C2—C3	−1.5 (4)	N2—C7—N1—C1	−11.0 (4)
N1—C1—C2—C3	−178.6 (2)	S1—C7—N1—C1	170.1 (2)
C1—C2—C3—C4	1.3 (4)	C6—C1—N1—C7	130.0 (3)
C2—C3—C4—C5	0.1 (4)	C2—C1—N1—C7	−52.9 (4)
C3—C4—C5—C6	−1.4 (4)	N1—C7—N2—C8	−177.1 (2)

C2—C1—C6—C5	0.3 (4)	S1—C7—N2—C8	1.8 (4)
N1—C1—C6—C5	177.4 (2)	C8^i—C8—N2—C7	80.6 (4)
C4—C5—C6—C1	1.2 (4)		

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

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1*N*···S1^{ii}	0.88	2.57	3.379 (2)	153

Symmetry code: (ii) −*x*+3/2, *y*+1/2, *z*.