

# 1,1'-Diphenyl-3,3'-(*p*-phenylene-dicarbonyl)dithiourea

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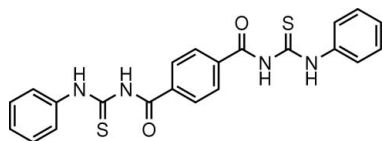
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Key indicators: single-crystal X-ray study;  $T = 273$  K; mean  $\sigma(\text{C}-\text{C}) = 0.004$  Å;  $R$  factor = 0.051;  $wR$  factor = 0.113; data-to-parameter ratio = 13.3.

The molecule of the title compound,  $\text{C}_{22}\text{H}_{18}\text{N}_4\text{O}_2\text{S}_2$ , lies across a crystallographic inversion centre. The central benzene ring forms dihedral angles of 29.39 (9) and 79.11 (12)°, respectively, with the thiourea unit and the terminal phenyl ring. Intramolecular  $\text{N}-\text{H}\cdots\text{O}$  hydrogen bonds generate two  $S(6)$  ring motifs. In the crystal, molecules are linked into chains along  $[1\bar{1}0]$  by intermolecular  $\text{N}-\text{H}\cdots\text{S}$  hydrogen bonds.

## Related literature

For general background and crystal structures of thiourea derivatives, see: Dong *et al.* (2006); Hassan *et al.* (2008); Yamin & Hassan (2004). For bond-length data, see: Allen *et al.* (1987).



## Experimental

### Crystal data

$\text{C}_{22}\text{H}_{18}\text{N}_4\text{O}_2\text{S}_2$   
 $M_r = 434.52$   
Triclinic,  $P\bar{1}$   
 $a = 5.769$  (2) Å

$b = 7.919$  (3) Å  
 $c = 11.534$  (4) Å  
 $\alpha = 75.961$  (10)°  
 $\beta = 87.000$  (8)°

$\gamma = 89.861$  (8)°  
 $V = 510.5$  (3) Å<sup>3</sup>  
 $Z = 1$   
Mo  $K\alpha$  radiation

$\mu = 0.29$  mm<sup>-1</sup>  
 $T = 273$  K  
 $0.23 \times 0.11 \times 0.05$  mm

### Data collection

Bruker SMART APEX CCD area-detector diffractometer  
Absorption correction: multi-scan (SADABS; Bruker, 2000)  
 $T_{\min} = 0.937$ ,  $T_{\max} = 0.986$

5484 measured reflections  
1809 independent reflections  
1503 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.030$

### Refinement

$R[F^2 > 2\sigma(F^2)] = 0.051$   
 $wR(F^2) = 0.113$   
 $S = 1.13$   
1809 reflections

136 parameters  
H-atom parameters constrained  
 $\Delta\rho_{\text{max}} = 0.25$  e Å<sup>-3</sup>  
 $\Delta\rho_{\text{min}} = -0.16$  e Å<sup>-3</sup>

Table 1

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$\text{N1}-\text{H1A}\cdots\text{O1}$	0.86	1.94	2.644 (3)	138
$\text{N2}-\text{H2A}\cdots\text{S1}^i$	0.86	2.62	3.446 (3)	160

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

Data collection: SMART (Bruker, 2000); cell refinement: SAINT (Bruker, 2000); data reduction: SAINT program(s) used to solve structure: SHELXS97 (Sheldrick, 2008); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008); molecular graphics: SHELXTL (Sheldrick, 2008); software used to prepare material for publication: SHELXTL and PLATON (Spek, 2009).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: CI5010).

## References

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**supplementary materials**

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## 1,1'-Diphenyl-3,3'-(*p*-phenylenedicarbonyl)dithiourea

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### Comment

The asymmetric unit of the title compound contains one-half of the molecule the other half being generated by the crystallographic inversion centre (Fig. 1). The thiourea fragment (S1/O1/N1/N2/C6/C7/C8) is planar, with atom C8 has the maximum deviation of 0.038 (2) Å from the mean plane. The dihedral angle between the central bridging benzene ring and the thiourea unit is 29.39 (9)° and that between the two benzene rings is 79.11 (12)°. The carbonyl and N-H groups are involved in intramolecular N—H···O hydrogen bonding resulting in the formation of two six-membered rings viz. C7/N2/C8/O1/H1A/N1 and C7A/N2A/C8A/O1A/H1AA/N1A. The C=O bond length of 1.220 (3) Å is longer than the average C=O bond length (1.200 Å). These features are similar to those observed in the structure of *N*-benzoyl-*N'*-(3-pyridyl)thiourea (Dong *et al.*, 2006). Bond lengths are in normal ranges (Allen *et al.*, 1987).

In the crystal structure, intermolecular N—H···S hydrogen bonds (Table 1) link the molecules into a chain along the [1 $\bar{1}$ 0] (Fig 2).

### Experimental

The title compound was synthesized according to a previously reported method (Hassan *et al.*, 2008) with some modification. Terephthaloyl chloride (1.015 g, 0.5 mmol) was added to ammonium thiocyanate (0.770 g, 1 mmol) in tetrahydrofuran and the contents were stirred for 10 min. The precipitated ammonium chloride was removed by filtration and then aniline (1.0 ml, 1 mmol) in methanol was added dropwise. The mixture was refluxed for 5 h and the black coloured solution was dried using an evaporator before it was washed with cool methanol. Yellow crystals of the title compound were obtained by recrystallization from DMF.

### Refinement

H atoms were positioned geometrically [N-H = 0.86 Å and C-H = 0.93 Å] and allowed to ride on their parent atoms, with  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C},\text{N})$ .

### Figures

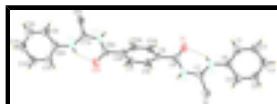


Fig. 1. The molecular structure of the title compound, with displacement ellipsoids drawn at the 50% probability level. Atoms labelled with the suffix A are generated by the symmetry operation (2-x, -y, 1-z).

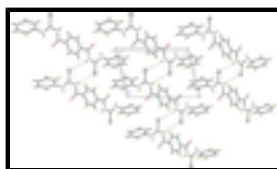


Fig. 2. Crystal packing of of the title compound, viewed down the *a* axis. Hydrogen bonds are shown as dashed lines.

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### Crystal data

$C_{22}H_{18}N_4O_2S_2$	$Z = 1$
$M_r = 434.52$	$F(000) = 226$
Triclinic, <i>PT</i>	$D_x = 1.413 \text{ Mg m}^{-3}$
Hall symbol: -P 1	Mo $K\alpha$ radiation, $\lambda = 0.71073 \text{ \AA}$
$a = 5.769 (2) \text{ \AA}$	Cell parameters from 1272 reflections
$b = 7.919 (3) \text{ \AA}$	$\theta = 1.8\text{--}25.0^\circ$
$c = 11.534 (4) \text{ \AA}$	$\mu = 0.29 \text{ mm}^{-1}$
$\alpha = 75.961 (10)^\circ$	$T = 273 \text{ K}$
$\beta = 87.000 (8)^\circ$	Plate, yellow
$\gamma = 89.861 (8)^\circ$	$0.23 \times 0.11 \times 0.05 \text{ mm}$
$V = 510.5 (3) \text{ \AA}^3$	

### Data collection

Bruker SMART APEX CCD area-detector diffractometer	1809 independent reflections
Radiation source: fine-focus sealed tube graphite	1503 reflections with $I > 2\sigma(I)$
$\omega$ scan	$R_{\text{int}} = 0.030$
Absorption correction: multi-scan ( <i>SADABS</i> ; Bruker, 2000)	$\theta_{\text{max}} = 25.0^\circ$ , $\theta_{\text{min}} = 1.8^\circ$
$T_{\text{min}} = 0.937$ , $T_{\text{max}} = 0.986$	$h = -6 \rightarrow 6$
5484 measured reflections	$k = -9 \rightarrow 9$
	$l = -13 \rightarrow 13$

### Refinement

Refinement on $F^2$	Primary atom site location: structure-invariant direct methods
Least-squares matrix: full	Secondary atom site location: difference Fourier map
$R[F^2 > 2\sigma(F^2)] = 0.051$	Hydrogen site location: inferred from neighbouring sites
$wR(F^2) = 0.113$	H-atom parameters constrained
$S = 1.13$	$w = 1/[\sigma^2(F_o^2) + (0.0449P)^2 + 0.1485P]$
1809 reflections	where $P = (F_o^2 + 2F_c^2)/3$
136 parameters	$(\Delta/\sigma)_{\text{max}} = 0.001$
0 restraints	$\Delta\rho_{\text{max}} = 0.25 \text{ e \AA}^{-3}$
	$\Delta\rho_{\text{min}} = -0.16 \text{ e \AA}^{-3}$

### 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 ( $\text{\AA}^2$ )*

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
S1	0.32753 (13)	0.52539 (9)	0.65718 (6)	0.0563 (3)
N1	0.2814 (3)	0.2027 (3)	0.79479 (17)	0.0451 (5)
H1A	0.3202	0.0953	0.8057	0.054*
N2	0.5449 (3)	0.2421 (2)	0.63257 (16)	0.0402 (5)
H2A	0.6037	0.3126	0.5690	0.048*
O1	0.5453 (3)	-0.0411 (2)	0.73721 (17)	0.0647 (6)
C1	0.1594 (5)	0.1854 (3)	1.0006 (2)	0.0506 (7)
H1B	0.2946	0.1251	1.0236	0.061*
C2	-0.0015 (5)	0.2172 (4)	1.0865 (2)	0.0580 (8)
H2B	0.0274	0.1796	1.1672	0.070*
C3	-0.2010 (5)	0.3030 (4)	1.0531 (3)	0.0570 (8)
H3A	-0.3086	0.3232	1.1111	0.068*
C4	-0.2439 (5)	0.3599 (4)	0.9342 (3)	0.0582 (8)
H4A	-0.3807	0.4184	0.9119	0.070*
C5	-0.0854 (4)	0.3310 (3)	0.8470 (2)	0.0504 (7)
H5A	-0.1148	0.3696	0.7664	0.060*
C6	0.1173 (4)	0.2439 (3)	0.8812 (2)	0.0413 (6)
C7	0.3798 (4)	0.3128 (3)	0.6997 (2)	0.0392 (6)
C8	0.6254 (4)	0.0747 (3)	0.6550 (2)	0.0416 (6)
C9	0.8197 (4)	0.0410 (3)	0.5729 (2)	0.0366 (5)
C10	0.9840 (4)	0.1665 (3)	0.5176 (2)	0.0424 (6)
H10A	0.9741	0.2781	0.5300	0.051*
C11	1.1621 (4)	0.1265 (3)	0.4442 (2)	0.0420 (6)
H11A	1.2700	0.2117	0.4063	0.063*

*Atomic displacement parameters ( $\text{\AA}^2$ )*

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
S1	0.0734 (5)	0.0418 (4)	0.0480 (4)	0.0108 (3)	0.0225 (3)	-0.0049 (3)
N1	0.0520 (13)	0.0393 (11)	0.0402 (12)	0.0059 (9)	0.0153 (10)	-0.0063 (9)
N2	0.0425 (11)	0.0406 (11)	0.0337 (11)	0.0043 (9)	0.0123 (9)	-0.0046 (9)
O1	0.0729 (13)	0.0485 (11)	0.0597 (12)	0.0131 (9)	0.0335 (10)	0.0042 (10)
C1	0.0528 (16)	0.0529 (16)	0.0418 (15)	0.0031 (13)	0.0062 (12)	-0.0049 (12)
C2	0.0677 (19)	0.0633 (19)	0.0397 (15)	-0.0032 (15)	0.0129 (13)	-0.0097 (13)
C3	0.0584 (18)	0.0592 (18)	0.0540 (18)	-0.0055 (14)	0.0247 (14)	-0.0205 (14)
C4	0.0433 (16)	0.0655 (19)	0.067 (2)	0.0032 (13)	0.0102 (14)	-0.0221 (15)
C5	0.0451 (15)	0.0641 (18)	0.0419 (15)	0.0022 (13)	0.0032 (12)	-0.0137 (13)

## supplementary materials

C6	0.0410 (14)	0.0391 (14)	0.0430 (14)	-0.0015 (11)	0.0105 (11)	-0.0110 (11)
C7	0.0384 (13)	0.0445 (14)	0.0346 (13)	0.0039 (11)	0.0027 (10)	-0.0106 (11)
C8	0.0419 (14)	0.0419 (14)	0.0386 (14)	0.0050 (11)	0.0056 (11)	-0.0070 (12)
C9	0.0368 (13)	0.0406 (13)	0.0318 (12)	0.0052 (10)	-0.0009 (10)	-0.0079 (10)
C10	0.0437 (14)	0.0376 (14)	0.0462 (15)	0.0032 (11)	0.0040 (11)	-0.0124 (11)
C11	0.0391 (13)	0.0401 (14)	0.0439 (14)	-0.0001 (10)	0.0086 (11)	-0.0068 (11)

### Geometric parameters ( $\text{\AA}$ , $^\circ$ )

S1—C7	1.667 (2)	C3—C4	1.372 (4)
N1—C7	1.327 (3)	C3—H3A	0.93
N1—C6	1.433 (3)	C4—C5	1.383 (3)
N1—H1A	0.86	C4—H4A	0.93
N2—C8	1.373 (3)	C5—C6	1.383 (3)
N2—C7	1.396 (3)	C5—H5A	0.93
N2—H2A	0.86	C8—C9	1.495 (3)
O1—C8	1.220 (3)	C9—C10	1.388 (3)
C1—C6	1.376 (4)	C9—C11 <sup>i</sup>	1.390 (3)
C1—C2	1.389 (4)	C10—C11	1.382 (3)
C1—H1B	0.93	C10—H10A	0.93
C2—C3	1.361 (4)	C11—C9 <sup>i</sup>	1.390 (3)
C2—H2B	0.93	C11—H11A	0.93
C7—N1—C6	126.8 (2)	C4—C5—H5A	120.4
C7—N1—H1A	116.6	C1—C6—C5	120.3 (2)
C6—N1—H1A	116.6	C1—C6—N1	118.3 (2)
C8—N2—C7	128.3 (2)	C5—C6—N1	121.3 (2)
C8—N2—H2A	115.8	N1—C7—N2	115.9 (2)
C7—N2—H2A	115.8	N1—C7—S1	125.62 (18)
C6—C1—C2	119.5 (3)	N2—C7—S1	118.42 (17)
C6—C1—H1B	120.2	O1—C8—N2	122.6 (2)
C2—C1—H1B	120.2	O1—C8—C9	121.2 (2)
C3—C2—C1	120.4 (3)	N2—C8—C9	116.2 (2)
C3—C2—H2B	119.8	C10—C9—C11 <sup>i</sup>	119.5 (2)
C1—C2—H2B	119.8	C10—C9—C8	123.1 (2)
C2—C3—C4	120.1 (2)	C11 <sup>i</sup> —C9—C8	117.4 (2)
C2—C3—H3A	119.9	C11—C10—C9	120.3 (2)
C4—C3—H3A	119.9	C11—C10—H10A	119.8
C3—C4—C5	120.6 (3)	C9—C10—H10A	119.8
C3—C4—H4A	119.7	C10—C11—C9 <sup>i</sup>	120.1 (2)
C5—C4—H4A	119.7	C10—C11—H11A	119.9
C6—C5—C4	119.2 (3)	C9 <sup>i</sup> —C11—H11A	119.9
C6—C5—H5A	120.4		

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

### Hydrogen-bond geometry ( $\text{\AA}$ , $^\circ$ )

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N1—H1A $\cdots$ O1	0.86	1.94	2.644 (3)	138

N2—H2A...S1<sup>ii</sup> 0.86 2.62 3.446 (3) 160  
 Symmetry codes: (ii)  $-x+1, -y+1, -z+1$ .

Fig. 1

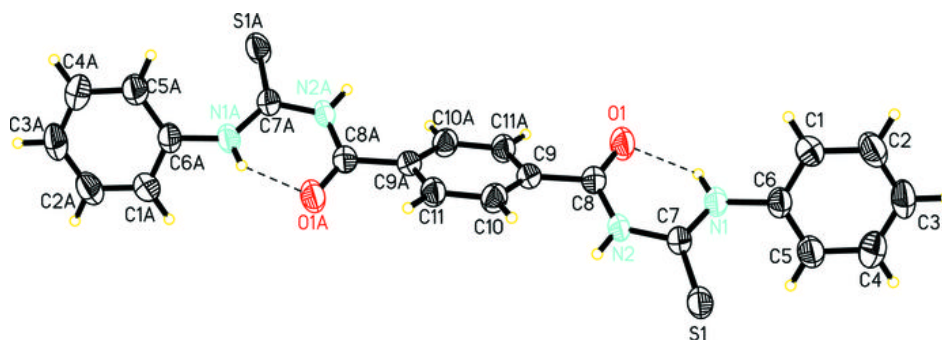


Fig. 2

