organic compounds

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

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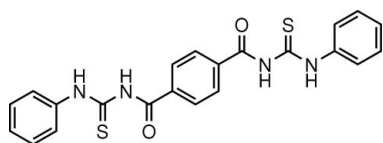Correspondence e-mail: mbkassim@ukm.my

The molecule of the title compound, $C_{22}H_{18}N_4O_2S_2$, 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 N—H···O hydrogen bonds generate two $S(6)$ ring motifs. In the crystal, molecules are linked into chains along [1$\bar{1}$0] by intermolecular N—H···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

$C_{22}H_{18}N_4O_2S_2$	b = 7.919 (3) Å
M_r = 434.52	c = 11.534 (4) Å
Triclinic, $P\bar{1}$	α = 75.961 (10)°
a = 5.769 (2) Å	β = 87.000 (8)°
γ = 89.861 (8)°	μ = 0.29 mm^{-1}
V = 510.5 (3) Å^3	T = 273 K
Z = 1	0.23 × 0.11 × 0.05 mm
Mo $K\alpha$ radiation	

Data collection

Bruker SMART APEX CCD area-detector diffractometer	5484 measured reflections
	1809 independent reflections
Absorption correction: multi-scan (*SADABS*; Bruker, 2000)	1503 reflections with $I > 2\sigma(I)$
T_{min} = 0.937, T_{max} = 0.986	R_{int} = 0.030

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.051	136 parameters
$wR(F^2)$ = 0.113	H-atom parameters constrained
S = 1.13	$\Delta\rho_{max}$ = 0.25 e Å^{-3}
1809 reflections	$\Delta\rho_{min}$ = −0.16 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1A···O1	0.86	1.94	2.644 (3)	138
N2—H2A···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).

References

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supporting information

1,1′-Diphenyl-3,3′-(*p*-phenylenedicarbonyl)dithiourea

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S1. 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).

S2. 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 a evaporator before it was washed with cool methanol. Yellow crystals of the title compound were obtained by recrystallization from DMF.

S3. Refinement

H atoms were positioned geometrically [N-H = 0.86 Å and C-H = 0.93Å] and allowed to ride on their parent atoms, with $U_{\mathrm{iso}}(\mathrm{H}) = 1.2U_{\mathrm{eq}}(\mathrm{C,N})$.
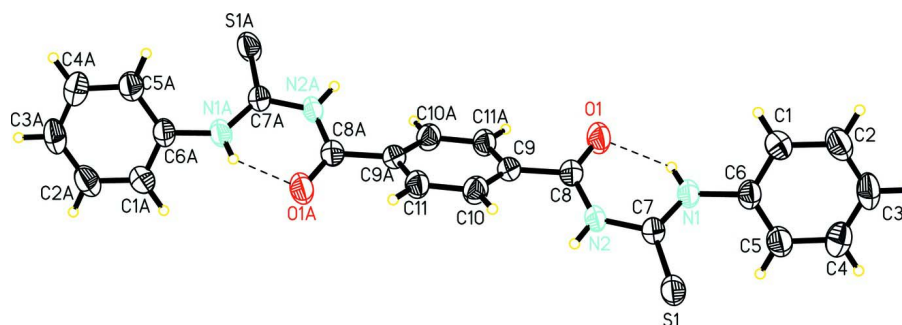
Figure 1

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).
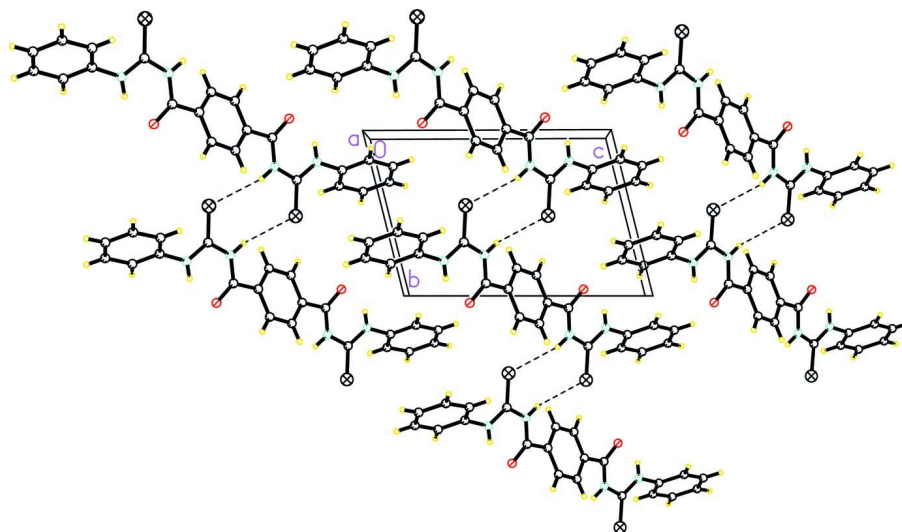
Figure 2

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, $P\bar{1}$	$D_x = 1.413$ Mg m^{-3}
Hall symbol: -P 1	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
$a = 5.769$ (2) Å	Cell parameters from 1272 reflections
$b = 7.919$ (3) Å	$\theta = 1.8$–25.0°
$c = 11.534$ (4) Å	$\mu = 0.29$ mm^{-1}
$\alpha = 75.961$ (10)°	$T = 273$ K
$\beta = 87.000$ (8)°	Plate, yellow
$\gamma = 89.861$ (8)°	$0.23 \times 0.11 \times 0.05$ mm
$V = 510.5$ (3) Å^3	

Data collection

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

Refinement

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

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^i	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^i	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—C11ⁱ	119.5 (2)
C1—C2—H2B	119.8	C10—C9—C8	123.1 (2)
C2—C3—C4	120.1 (2)	C11ⁱ—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—C9ⁱ	120.1 (2)
C5—C4—H4A	119.7	C10—C11—H11A	119.9
C6—C5—C4	119.2 (3)	C9ⁱ—C11—H11A	119.9
C6—C5—H5A	120.4		

Symmetry code: (i) −*x*+2, −*y*, −*z*+1.

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1*A*···O1	0.86	1.94	2.644 (3)	138
N2—H2*A*···S1ⁱⁱ	0.86	2.62	3.446 (3)	160

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