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## Structure Reports

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## 3,3'-Dibenzoyl-1,1'-(butane-1,4-diyl)-dithiourea

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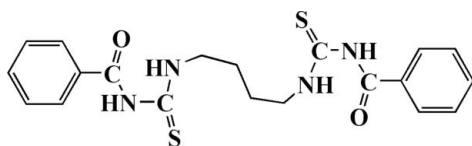
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Key indicators: single-crystal X-ray study;  $T = 298$  K; mean  $\sigma(\text{C}-\text{C}) = 0.004$  Å;  $R$  factor = 0.057;  $wR$  factor = 0.107; data-to-parameter ratio = 13.7.

In the centrosymmetric title compound,  $\text{C}_{20}\text{H}_{22}\text{N}_4\text{O}_2\text{S}_2$ , the carbonyl group forms an intramolecular hydrogen bond with the NH group attached to the butanediyl linker, resulting in a six-membered ring. There are also intermolecular  $\text{C}-\text{H}\cdots\text{S}$  interactions in the crystal structure, and  $\pi-\pi$  interactions between phenyl groups [2.425 (3) Å].

## Related literature

For related literature, see: Breuzard *et al.* (2000); Burrows *et al.* (1997); Dong *et al.* (2006); Foss *et al.* (2004); Huang *et al.*, 2006; Nan *et al.* (2000); Teoh *et al.* (1999); Valdés-Martínez *et al.* (2004); Zhang *et al.* (2006).



## Experimental

## Crystal data

 $\text{C}_{20}\text{H}_{22}\text{N}_4\text{O}_2\text{S}_2$  $M_r = 414.54$ Monoclinic,  $P2_1/c$  $a = 6.0405$  (11) Å $b = 23.358$  (2) Å $c = 7.2877$  (13) Å $\beta = 104.018$  (2)° $V = 997.6$  (3) Å<sup>3</sup> $Z = 2$ Mo  $K\alpha$  radiation $\mu = 0.29$  mm<sup>-1</sup> $T = 298$  (2) K

0.22 × 0.16 × 0.07 mm

## Data collection

Bruker SMART CCD area-detector diffractometer

Absorption correction: multi-scan (SADABS; Sheldrick, 1996)

 $T_{\min} = 0.939$ ,  $T_{\max} = 0.980$ 

4845 measured reflections

1735 independent reflections

1044 reflections with  $I > 2\sigma(I)$  $R_{\text{int}} = 0.058$ 

## Refinement

 $R[F^2 > 2\sigma(F^2)] = 0.056$  $wR(F^2) = 0.106$  $S = 1.02$ 

1735 reflections

127 parameters

H-atom parameters constrained

 $\Delta\rho_{\text{max}} = 0.23$  e Å<sup>-3</sup> $\Delta\rho_{\text{min}} = -0.21$  e Å<sup>-3</sup>

Table 1

Hydrogen-bond geometry (Å, °).

$D-\text{H}\cdots A$	$D-\text{H}$	$\text{H}\cdots A$	$D\cdots A$	$D-\text{H}\cdots A$
$\text{N2}-\text{H2}\cdots\text{O1}$	0.86	2.06	2.717 (3)	133
$\text{C2}-\text{H2A}\cdots\text{S1}$	0.97	2.68	3.060 (3)	103
$\text{C2}-\text{H2B}\cdots\text{S1}^i$	0.97	2.72	3.468 (3)	134

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

Data collection: SMART (Siemens, 1996); cell refinement: SAINT (Siemens, 1996); data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 2008); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008); molecular graphics: SHELXTL (Version 5.1; Sheldrick, 2008); software used to prepare material for publication: SHELXTL.

This work was supported by the Foundation of the Education Department of Gansu Province (grant No. 0604-01) and the Qing Lan Talent Engineering Fund of Lanzhou Jiaotong University (grant No. QL-03-01A), which are gratefully acknowledged.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: HG2377).

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## supporting information

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## 3,3'-Dibenzoyl-1,1'-(butane-1,4-diyl)dithiourea

Yu-Jie Ding, Xi-Bin Chang, Xiao-Qing Yang and Wen-Kui Dong

### S1. Comment

Acylthioureas have been the subject of extensive investigation because of their biological activity and their ability to coordinate strongly with metal ions (Teoh *et al.*, 1999; Huang *et al.*, 2006; Foss *et al.*, 2004). Some thioureas are organic catalysts in the metal-catalyzed asymmetric reduction of carbonyl compounds and carbonylative cyclization of *o*-hydroxyarylacetylenes (Nan *et al.*, 2000; Breuzard *et al.*, 2000). In recent years, thiourea derivatives have been studied because they are excellent H bonding donors and acceptors (Zhang *et al.*, 2006; Valdés-Martínez *et al.*, 2004), and readily form an intramolecular hydrogen bonding between the benzoyl (CO) and the N—H group (Dong *et al.*, 2006). They also easily form intermolecular hydrogen bonds, which can be applied in the design and synthesis of three-dimension supramolecular structure (Burrows *et al.*, 1997). Here we report synthesis and crystal structure of N, N'-(1, 4-tetramethylene)bisbenzoylthiourea (I), C<sub>20</sub>H<sub>22</sub>N<sub>4</sub>O<sub>2</sub>S<sub>2</sub>.

The crystal structure of (I) consists of discrete molecules. The carbonyl group forms an intramolecular hydrogen bond with the N2—H2 group, which forms a six-membered ring (C4/N1/C1/N2/H2/O1) structure, the H2...O1 bond length is 2.055 (3) Å. This is similar to the situation found in the structure of *N*-benzoyl-*N'*-(3-pyridyl)thiourea (Dong *et al.*, 2006). There is intermolecular hydrogen bonding between N2—H2 and the C?S group of another molecule, the H2...S1(*x* + 1, *y*, *z*) bond length is 2.906 (3) Å. The C?O bond length of 1.223 (3) Å is longer than the average C?O bond length (1.200 Å), which is due to intramolecular hydrogen bonding. The torsion angles of C2—N2—C1—N1 and C2—N2—C1—S1 are 178.3 (2) and -0.9 (4)°. There are  $\pi$ - $\pi$  interactions between phenyl groups in the crystal lattice.

### S2. Experimental

Benzoyl chloride (1.41 g, 10 mmol) was reacted with ammonium thiocyanate (1.14 g, 15 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (25 ml) solution under solid-liquid phase transfer catalysis, using polyethylene glycol-400 (0.18 g) as the catalyst, to give the corresponding benzoyl isothiocyanate. Then a solution of 1,4-butylenediamine (0.40 g, 4.5 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (15 ml) was added dropwise to benzoyl isothiocyanate, to give the title compound. Yield, 81.8%. m.p. 196–198 °C. Anal. Calc. for C<sub>20</sub>H<sub>22</sub>N<sub>4</sub>O<sub>2</sub>S<sub>2</sub> (%): C, 57.97; H, 5.31; N, 13.53. Found: C, 57.90; H, 5.45; N, 13.35. Selected IR data (cm<sup>-1</sup>, KBr pellet): 3416, 3222 ( $\nu$  NH), 1672 ( $\nu$  C?O), 1146 ( $\nu$  C?S). <sup>1</sup>H NMR (200 MHz, DMSO-d<sub>6</sub>,  $\delta$ , p.p.m.): 1.71 (t, 4H, CH<sub>2</sub>); 3.69 (t, 4H, CH<sub>2</sub>); 7.48–7.93 (m, 10H, C<sub>6</sub>H<sub>5</sub>); 10.95 (s, 1H, NH); 11.06 (s, 1H, NH). A DMF solution of the title compound was placed in a diethyl ether atmosphere, after several days, along with diffusion of diethyl ether into the DMF solution of the title compound, colorless block-shaped single crystals suitable for X-ray crystallographic analysis were obtained.

### S3. Refinement

Non-H atoms were refined anisotropically. H atoms were treated as riding atoms with distances C—H = 0.97 (CH<sub>2</sub>), or 0.93 Å (CH), N—H = 0.86 Å, and  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$  and  $1.5U_{\text{eq}}(\text{N})$ .

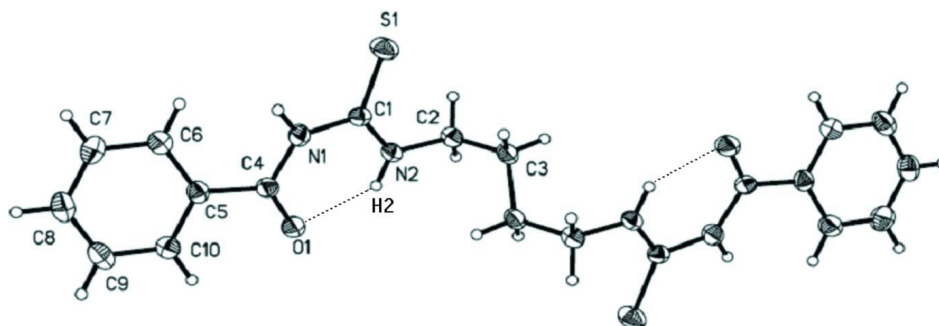


Figure 1

The molecular structure of (I)

### 3,3'-Dibenzoyl-1,1'-(butane-1,4-diyl)dithiourea

#### Crystal data

$C_{20}H_{22}N_4O_2S_2$

$M_r = 414.54$

Monoclinic,  $P2_1/c$

Hall symbol: -P 2ybc

$a = 6.0405$  (11) Å

$b = 23.358$  (2) Å

$c = 7.2877$  (13) Å

$\beta = 104.018$  (2)°

$V = 997.6$  (3) Å<sup>3</sup>

$Z = 2$

$F(000) = 436$

$D_x = 1.380$  Mg m<sup>-3</sup>

Melting point = 469–471 K

Mo  $K\alpha$  radiation,  $\lambda = 0.71073$  Å

Cell parameters from 1545 reflections

$\theta = 2.9$ – $27.5^\circ$

$\mu = 0.29$  mm<sup>-1</sup>

$T = 298$  K

Block, colourless

$0.22 \times 0.16 \times 0.07$  mm

#### Data collection

Bruker SMART CCD area-detector  
diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

$\varphi$  and  $\omega$  scans

Absorption correction: multi-scan

(*SADABS*; Sheldrick, 1996)

$T_{\min} = 0.939$ ,  $T_{\max} = 0.980$

4845 measured reflections

1735 independent reflections

1044 reflections with  $I > 2\sigma(I)$

$R_{\text{int}} = 0.058$

$\theta_{\max} = 25.0^\circ$ ,  $\theta_{\min} = 1.7^\circ$

$h = -7 \rightarrow 7$

$k = -27 \rightarrow 21$

$l = -8 \rightarrow 7$

#### Refinement

Refinement on  $F^2$

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.056$

$wR(F^2) = 0.106$

$S = 1.02$

1735 reflections

127 parameters

0 restraints

Primary atom site location: structure-invariant  
direct methods

Secondary atom site location: difference Fourier  
map

Hydrogen site location: inferred from  
neighbouring sites

H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0375P)^2 + 0.093P]$

where  $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} < 0.001$

$\Delta\rho_{\max} = 0.23$  e Å<sup>-3</sup>

$\Delta\rho_{\min} = -0.21$  e Å<sup>-3</sup>

*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>	$U_{\text{iso}}^*/U_{\text{eq}}$
N1	0.6333 (4)	0.33193 (10)	0.2464 (3)	0.0436 (7)
H1	0.4996	0.3174	0.2342	0.052*
N2	0.8393 (4)	0.41571 (9)	0.2530 (3)	0.0378 (6)
H2	0.9588	0.3944	0.2747	0.045*
O1	1.0080 (4)	0.30751 (8)	0.3060 (3)	0.0556 (7)
S1	0.39076 (13)	0.42652 (4)	0.19513 (14)	0.0579 (3)
C1	0.6387 (5)	0.39150 (12)	0.2345 (4)	0.0367 (7)
C2	0.8669 (5)	0.47772 (12)	0.2383 (4)	0.0403 (8)
H2A	0.7351	0.4931	0.1482	0.048*
H2B	1.0004	0.4853	0.1902	0.048*
C3	0.8930 (4)	0.50817 (12)	0.4263 (4)	0.0415 (8)
H3A	0.8946	0.5491	0.4051	0.050*
H3B	0.7612	0.4996	0.4755	0.050*
C4	0.8082 (5)	0.29268 (13)	0.2746 (4)	0.0395 (8)
C5	0.7380 (5)	0.23119 (12)	0.2626 (4)	0.0383 (8)
C6	0.5157 (6)	0.21226 (13)	0.1896 (5)	0.0530 (9)
H6	0.3997	0.2387	0.1462	0.064*
C7	0.4663 (6)	0.15458 (15)	0.1811 (5)	0.0617 (10)
H7	0.3171	0.1425	0.1316	0.074*
C8	0.6341 (6)	0.11496 (14)	0.2445 (5)	0.0557 (10)
H8	0.5993	0.0761	0.2394	0.067*
C9	0.8531 (6)	0.13299 (14)	0.3154 (5)	0.0555 (9)
H9	0.9681	0.1062	0.3581	0.067*
C10	0.9057 (5)	0.19086 (13)	0.3241 (4)	0.0462 (9)
H10	1.0558	0.2026	0.3720	0.055*

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

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
N1	0.0352 (14)	0.0346 (15)	0.060 (2)	−0.0048 (12)	0.0101 (13)	−0.0022 (13)
N2	0.0309 (14)	0.0340 (14)	0.0476 (17)	0.0051 (11)	0.0077 (12)	−0.0024 (12)
O1	0.0374 (13)	0.0408 (13)	0.0810 (18)	−0.0008 (10)	−0.0005 (12)	0.0001 (12)
S1	0.0363 (5)	0.0507 (5)	0.0883 (8)	0.0062 (4)	0.0181 (5)	0.0070 (5)
C1	0.0325 (17)	0.0413 (18)	0.036 (2)	0.0030 (14)	0.0078 (14)	0.0004 (15)
C2	0.0375 (17)	0.0373 (18)	0.047 (2)	0.0039 (14)	0.0125 (15)	0.0036 (16)
C3	0.0386 (17)	0.0299 (17)	0.055 (2)	0.0042 (13)	0.0102 (16)	0.0017 (16)

C4	0.043 (2)	0.0399 (19)	0.033 (2)	0.0048 (15)	0.0035 (16)	-0.0001 (15)
C5	0.0455 (19)	0.0358 (18)	0.034 (2)	0.0012 (15)	0.0108 (16)	-0.0009 (15)
C6	0.047 (2)	0.042 (2)	0.065 (3)	0.0019 (16)	0.0047 (18)	0.0009 (19)
C7	0.056 (2)	0.049 (2)	0.075 (3)	-0.0142 (18)	0.007 (2)	-0.005 (2)
C8	0.074 (3)	0.039 (2)	0.057 (3)	-0.0035 (19)	0.021 (2)	0.0001 (18)
C9	0.071 (3)	0.043 (2)	0.054 (3)	0.0150 (19)	0.018 (2)	0.0049 (18)
C10	0.044 (2)	0.044 (2)	0.048 (2)	0.0045 (16)	0.0070 (17)	-0.0015 (17)

*Geometric parameters (Å, °)*

N1—C4	1.376 (3)	C3—H3B	0.9700
N1—C1	1.395 (3)	C4—C5	1.494 (4)
N1—H1	0.8600	C5—C10	1.376 (4)
N2—C1	1.314 (3)	C5—C6	1.391 (4)
N2—C2	1.465 (3)	C6—C7	1.378 (4)
N2—H2	0.8600	C6—H6	0.9300
O1—C4	1.223 (3)	C7—C8	1.368 (4)
S1—C1	1.669 (3)	C7—H7	0.9300
C2—C3	1.518 (4)	C8—C9	1.365 (4)
C2—H2A	0.9700	C8—H8	0.9300
C2—H2B	0.9700	C9—C10	1.387 (4)
C3—C3 <sup>i</sup>	1.516 (5)	C9—H9	0.9300
C3—H3A	0.9700	C10—H10	0.9300
C4—N1—C1	130.2 (2)	O1—C4—N1	121.8 (3)
C4—N1—H1	114.9	O1—C4—C5	122.4 (3)
C1—N1—H1	114.9	N1—C4—C5	115.8 (3)
C1—N2—C2	122.4 (2)	C10—C5—C6	118.2 (3)
C1—N2—H2	118.8	C10—C5—C4	117.6 (3)
C2—N2—H2	118.8	C6—C5—C4	124.2 (3)
N2—C1—N1	117.2 (2)	C7—C6—C5	120.4 (3)
N2—C1—S1	125.0 (2)	C7—C6—H6	119.8
N1—C1—S1	117.8 (2)	C5—C6—H6	119.8
N2—C2—C3	112.7 (2)	C8—C7—C6	120.8 (3)
N2—C2—H2A	109.1	C8—C7—H7	119.6
C3—C2—H2A	109.1	C6—C7—H7	119.6
N2—C2—H2B	109.1	C9—C8—C7	119.3 (3)
C3—C2—H2B	109.1	C9—C8—H8	120.3
H2A—C2—H2B	107.8	C7—C8—H8	120.3
C3 <sup>i</sup> —C3—C2	114.0 (3)	C8—C9—C10	120.6 (3)
C3 <sup>i</sup> —C3—H3A	108.8	C8—C9—H9	119.7
C2—C3—H3A	108.8	C10—C9—H9	119.7
C3 <sup>i</sup> —C3—H3B	108.8	C5—C10—C9	120.7 (3)
C2—C3—H3B	108.8	C5—C10—H10	119.7
H3A—C3—H3B	107.7	C9—C10—H10	119.7
C2—N2—C1—N1	178.3 (2)	O1—C4—C5—C6	-166.1 (3)
C2—N2—C1—S1	-0.9 (4)	N1—C4—C5—C6	13.4 (4)

C4—N1—C1—N2	-0.3 (4)	C10—C5—C6—C7	0.5 (5)
C4—N1—C1—S1	179.0 (2)	C4—C5—C6—C7	179.0 (3)
C1—N2—C2—C3	88.5 (3)	C5—C6—C7—C8	0.2 (5)
N2—C2—C3—C3 <sup>i</sup>	64.4 (4)	C6—C7—C8—C9	-0.6 (5)
C1—N1—C4—O1	4.7 (5)	C7—C8—C9—C10	0.3 (5)
C1—N1—C4—C5	-174.8 (3)	C6—C5—C10—C9	-0.8 (5)
O1—C4—C5—C10	12.4 (4)	C4—C5—C10—C9	-179.4 (3)
N1—C4—C5—C10	-168.1 (3)	C8—C9—C10—C5	0.4 (5)

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

*Hydrogen-bond geometry (Å, °)*

<i>D—H...A</i>	<i>D—H</i>	<i>H...A</i>	<i>D...A</i>	<i>D—H...A</i>
N2—H2...O1	0.86	2.06	2.717 (3)	133
C2—H2A...S1	0.97	2.68	3.060 (3)	103
C2—H2B...S1 <sup>ii</sup>	0.97	2.72	3.468 (3)	134

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