

Redetermination of *N,N'*-bis(4-chlorophenyl)thiourea at 173 KB. K. Sarojini,<sup>a</sup> B. Narayana,<sup>b</sup> M. T. Swamy,<sup>c</sup> H. S. Yathirajan<sup>d</sup> and Michael Bolte<sup>e\*</sup>

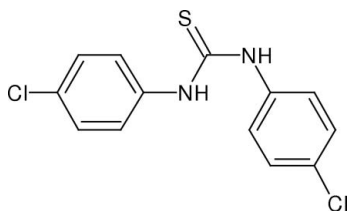
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Key indicators: single-crystal X-ray study;  $T = 173$  K; mean  $\sigma(\text{C}-\text{C}) = 0.002$  Å;  $R$  factor = 0.032;  $wR$  factor = 0.083; data-to-parameter ratio = 18.1.

The structure of the title compound,  $\text{C}_{13}\text{H}_{10}\text{Cl}_2\text{N}_2\text{S}$ , has already been determined at room temperature [Soriano-García, Chávez, Cedillo, Pérez & Hernández (2001). *Anal. Sci.* **17**, 799–800]. However, the positions of the H atoms were not provided. Thus, we present here the complete structure determined from data at low temperature (173 K). The molecules are connected *via* bifurcated  $\text{N}-\text{H}\cdots\text{S}$  hydrogen bonds to form zigzag chains running along the  $b$  axis. The title compound is isomorphous with 1,3-bis(4-bromophenyl)thiourea.

## Related literature

For related literature, see: Muhammed *et al.* (2007).

## Experimental

## Crystal data

$\text{C}_{13}\text{H}_{10}\text{Cl}_2\text{N}_2\text{S}$   
 $M_r = 297.19$   
 Monoclinic,  $P2_1/c$   
 $a = 13.8552$  (11) Å  
 $b = 7.1640$  (4) Å  
 $c = 14.1324$  (11) Å  
 $\beta = 103.290$  (6)°

$V = 1365.20$  (17) Å<sup>3</sup>  
 $Z = 4$   
 Mo  $K\alpha$  radiation  
 $\mu = 0.61$  mm<sup>-1</sup>  
 $T = 173$  (2) K  
 $0.37 \times 0.34 \times 0.32$  mm

## Data collection

Stoe IPDSII two-circle diffractometer  
 Absorption correction: multi-scan [MULABS (Spek, 2003; Blessing, 1995)]  
 $T_{\min} = 0.806$ ,  $T_{\max} = 0.829$

18732 measured reflections  
 3118 independent reflections  
 2828 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.042$

## Refinement

$R[F^2 > 2\sigma(F^2)] = 0.032$   
 $wR(F^2) = 0.083$   
 $S = 1.06$   
 3118 reflections  
 172 parameters

H atoms treated by a mixture of independent and constrained refinement  
 $\Delta\rho_{\max} = 0.43$  e Å<sup>-3</sup>  
 $\Delta\rho_{\min} = -0.48$  e Å<sup>-3</sup>

Table 1

Hydrogen-bond geometry (Å, °).

$D-\text{H}\cdots A$	$D-\text{H}$	$\text{H}\cdots A$	$D\cdots A$	$D-\text{H}\cdots A$
$\text{N1}-\text{H1}\cdots\text{S1}^i$	0.83 (2)	2.58 (2)	3.3787 (13)	159.5 (16)
$\text{N2}-\text{H2}\cdots\text{S1}^i$	0.85 (2)	2.50 (2)	3.3272 (13)	163.2 (18)

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

Data collection: *X-AREA* (Stoe & Cie, 2001); cell refinement: *X-AREA*; data reduction: *X-AREA*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2003); software used to prepare material for publication: *SHELXL97*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: AT2379).

## References

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**supplementary materials**

*Acta Cryst.* (2007). E63, o3879 [ doi:10.1107/S1600536807040871 ]

## Redetermination of *N,N'*-bis(4-chlorophenyl)thiourea at 173 K

B. K. Sarojini, B. Narayana, M. T. Swamy, H. S. Yathirajan and M. Bolte

### Comment

The structure of the title compound, C<sub>13</sub>H<sub>10</sub>Cl<sub>2</sub>N<sub>2</sub>S, has already been determined at room temperature [Soriano-García, Chávez, Cedillo, Pérez & Hernández (2001). *Anal. Sci.* 17, 799–800]. However, the positions of the H atoms have not been provided. Thus, we present here the complete structure determined from data at low temperature.

The molecules are connected *via* bifurcated N—H...S hydrogen bonds to form zigzag chains running along the *b* axis. The title compound is isomorphous with 1,3-bis(4-bromophenyl)thiourea (Muhammed *et al.*, 2007).

### Experimental

4-Chloroaniline (2.07 g, 0.0081 mol) was refluxed with potassium thiocyanate (1.4 g, 0.0142 mol) in 30 ml water and 1.6 ml conc. HCl for 3 h. The reaction mixture was then cooled to room temperature and stirred overnight. The precipitated product was then filtered, washed with water, dried and recrystallized from (9:1) acetone and toluene mixture (m.p.: 417–419 K). Analysis for C<sub>13</sub>H<sub>10</sub>Cl<sub>2</sub>N<sub>2</sub>S: Found (Calculated): C 52.45 (52.54), H 3.32 (3.39), N 9.36 (9.43), S 10.70% (10.79%).

### Refinement

H atoms were found in a difference map, but those bonded to C were refined using a riding model with C—H = 0.95 Å and  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ . The H atoms bonded to N were freely refined.

### Figures

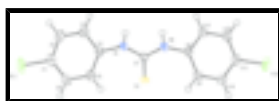


Fig. 1. Perspective view of the title compound with the atom numbering; displacement ellipsoids are at the 50% probability level.

### *N,N'*-bis(4-chlorophenyl)thiourea

#### Crystal data

C<sub>13</sub>H<sub>10</sub>Cl<sub>2</sub>N<sub>2</sub>S

$M_r = 297.19$

$F_{000} = 608$

$D_x = 1.446 \text{ Mg m}^{-3}$

# supplementary materials

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Monoclinic,  $P2_1/c$

Hall symbol: -P 2ybc

$a = 13.8552$  (11) Å

$b = 7.1640$  (4) Å

$c = 14.1324$  (11) Å

$\beta = 103.290$  (6)°

$V = 1365.20$  (17) Å<sup>3</sup>

$Z = 4$

Mo  $K\alpha$  radiation

$\lambda = 0.71073$  Å

Cell parameters from 17612 reflections

$\theta = 3.6$ – $27.7$ °

$\mu = 0.61$  mm<sup>-1</sup>

$T = 173$  (2) K

Block, colourless

$0.37 \times 0.34 \times 0.32$  mm

## Data collection

Stoe IPDS II two-circle diffractometer

Radiation source: fine-focus sealed tube

Monochromator: graphite

$T = 173$ (2) K

$\omega$  scans

Absorption correction: multi-scan [MULABS (Spek, 2003; Blessing, 1995)]

$T_{\min} = 0.806$ ,  $T_{\max} = 0.829$

18732 measured reflections

3118 independent reflections

2828 reflections with  $I > 2\sigma(I)$

$R_{\text{int}} = 0.042$

$\theta_{\text{max}} = 27.6$ °

$\theta_{\text{min}} = 3.6$ °

$h = -17 \rightarrow 17$

$k = -9 \rightarrow 9$

$l = -18 \rightarrow 17$

## Refinement

Refinement on  $F^2$

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.032$

$wR(F^2) = 0.083$

$S = 1.06$

3118 reflections

172 parameters

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

$$w = 1/[\sigma^2(F_o^2) + (0.0416P)^2 + 0.5812P]$$

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

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

$\Delta\rho_{\text{max}} = 0.43$  e Å<sup>-3</sup>

$\Delta\rho_{\text{min}} = -0.48$  e Å<sup>-3</sup>

Extinction correction: SHELXL97 (Sheldrick, 1997),

$$F_c^* = kF_c[1 + 0.001xF_c^2\lambda^3/\sin(2\theta)]^{-1/4}$$

Extinction coefficient: 0.0115 (13)

## 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  $F^2 > 2\text{sigma}(F^2)$  is used only for calculat-

ing  $R$ -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 ( $\text{\AA}^2$ )

	$x$	$y$	$z$	$U_{\text{iso}}^*/U_{\text{eq}}$
C11	0.86710 (4)	0.20429 (9)	0.48109 (4)	0.05742 (17)
C12	0.02930 (3)	0.21344 (9)	0.83408 (4)	0.05364 (16)
S1	0.41410 (2)	0.15822 (5)	0.60687 (2)	0.02176 (10)
N1	0.55058 (9)	0.41911 (17)	0.68187 (9)	0.0243 (2)
H1	0.5712 (13)	0.492 (3)	0.7280 (14)	0.034 (5)*
N2	0.40903 (9)	0.43015 (17)	0.73673 (9)	0.0248 (3)
H2	0.4436 (15)	0.501 (3)	0.7800 (16)	0.045 (6)*
C1	0.77329 (12)	0.2673 (2)	0.53935 (13)	0.0333 (3)
C2	0.79706 (11)	0.3009 (2)	0.63856 (13)	0.0349 (4)
H2A	0.8638	0.2923	0.6746	0.042*
C3	0.72165 (11)	0.3476 (2)	0.68460 (11)	0.0290 (3)
H3	0.7370	0.3706	0.7526	0.035*
C4	0.62372 (10)	0.36086 (18)	0.63133 (10)	0.0223 (3)
C5	0.60103 (11)	0.3290 (2)	0.53124 (10)	0.0253 (3)
H5	0.5345	0.3395	0.4947	0.030*
C6	0.67648 (12)	0.2815 (2)	0.48504 (11)	0.0300 (3)
H6	0.6617	0.2590	0.4170	0.036*
C7	0.45935 (9)	0.34474 (18)	0.67691 (9)	0.0197 (3)
C8	0.31635 (10)	0.37305 (19)	0.75578 (10)	0.0222 (3)
C9	0.23088 (11)	0.3522 (2)	0.68238 (10)	0.0301 (3)
H9	0.2331	0.3717	0.6164	0.036*
C10	0.14188 (11)	0.3024 (3)	0.70598 (12)	0.0345 (4)
H10	0.0835	0.2849	0.6562	0.041*
C11	0.13964 (11)	0.2786 (2)	0.80308 (12)	0.0318 (3)
C12	0.22385 (11)	0.3042 (2)	0.87692 (11)	0.0299 (3)
H12	0.2209	0.2901	0.9430	0.036*
C13	0.31273 (10)	0.3509 (2)	0.85273 (10)	0.0255 (3)
H13	0.3711	0.3677	0.9026	0.031*

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

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
C11	0.0447 (3)	0.0746 (4)	0.0649 (3)	0.0117 (2)	0.0372 (2)	0.0028 (3)
C12	0.0270 (2)	0.0809 (4)	0.0574 (3)	-0.0063 (2)	0.01892 (19)	0.0048 (3)
S1	0.02455 (17)	0.02253 (17)	0.01732 (16)	-0.00173 (12)	0.00302 (12)	-0.00205 (12)
N1	0.0254 (6)	0.0260 (6)	0.0227 (6)	-0.0047 (5)	0.0080 (5)	-0.0075 (5)
N2	0.0244 (6)	0.0275 (6)	0.0236 (6)	-0.0036 (5)	0.0080 (5)	-0.0071 (5)
C1	0.0322 (8)	0.0322 (8)	0.0419 (9)	0.0024 (6)	0.0220 (7)	0.0038 (7)
C2	0.0229 (7)	0.0401 (9)	0.0424 (9)	-0.0011 (6)	0.0093 (6)	0.0038 (7)
C3	0.0256 (7)	0.0331 (7)	0.0279 (7)	-0.0044 (6)	0.0054 (6)	-0.0003 (6)
C4	0.0237 (6)	0.0197 (6)	0.0251 (6)	-0.0020 (5)	0.0092 (5)	0.0003 (5)
C5	0.0269 (7)	0.0247 (7)	0.0251 (7)	0.0009 (5)	0.0076 (5)	0.0024 (5)

## supplementary materials

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C6	0.0379 (8)	0.0291 (7)	0.0272 (7)	0.0007 (6)	0.0160 (6)	0.0012 (6)
C7	0.0229 (6)	0.0207 (6)	0.0149 (5)	0.0008 (5)	0.0033 (5)	0.0029 (5)
C8	0.0223 (6)	0.0225 (6)	0.0225 (6)	0.0013 (5)	0.0070 (5)	-0.0019 (5)
C9	0.0263 (7)	0.0426 (8)	0.0206 (6)	0.0033 (6)	0.0040 (5)	0.0002 (6)
C10	0.0216 (7)	0.0493 (10)	0.0310 (8)	0.0022 (6)	0.0023 (6)	-0.0026 (7)
C11	0.0219 (7)	0.0387 (8)	0.0367 (8)	0.0014 (6)	0.0109 (6)	0.0001 (7)
C12	0.0305 (7)	0.0365 (8)	0.0247 (7)	0.0014 (6)	0.0105 (6)	0.0020 (6)
C13	0.0249 (6)	0.0301 (7)	0.0213 (6)	0.0012 (5)	0.0047 (5)	-0.0019 (5)

### *Geometric parameters (Å, °)*

C11—C1	1.7502 (15)	C4—C5	1.3955 (19)
C12—C11	1.7480 (15)	C5—C6	1.396 (2)
S1—C7	1.6950 (14)	C5—H5	0.9500
N1—C7	1.3586 (17)	C6—H6	0.9500
N1—C4	1.4297 (17)	C8—C9	1.391 (2)
N1—H1	0.83 (2)	C8—C13	1.3916 (19)
N2—C7	1.3588 (17)	C9—C10	1.396 (2)
N2—C8	1.4309 (17)	C9—H9	0.9500
N2—H2	0.85 (2)	C10—C11	1.390 (2)
C1—C2	1.386 (2)	C10—H10	0.9500
C1—C6	1.388 (2)	C11—C12	1.387 (2)
C2—C3	1.393 (2)	C12—C13	1.393 (2)
C2—H2A	0.9500	C12—H12	0.9500
C3—C4	1.3954 (19)	C13—H13	0.9500
C3—H3	0.9500		
C7—N1—C4	128.14 (12)	C5—C6—H6	120.3
C7—N1—H1	115.7 (12)	N1—C7—N2	113.31 (12)
C4—N1—H1	114.8 (12)	N1—C7—S1	123.65 (10)
C7—N2—C8	126.82 (12)	N2—C7—S1	122.99 (10)
C7—N2—H2	115.5 (14)	C9—C8—C13	120.31 (13)
C8—N2—H2	114.6 (14)	C9—C8—N2	122.50 (12)
C2—C1—C6	121.44 (14)	C13—C8—N2	117.05 (12)
C2—C1—C11	119.44 (13)	C8—C9—C10	119.78 (14)
C6—C1—C11	119.12 (13)	C8—C9—H9	120.1
C1—C2—C3	119.03 (15)	C10—C9—H9	120.1
C1—C2—H2A	120.5	C11—C10—C9	119.25 (14)
C3—C2—H2A	120.5	C11—C10—H10	120.4
C2—C3—C4	120.34 (14)	C9—C10—H10	120.4
C2—C3—H3	119.8	C12—C11—C10	121.38 (14)
C4—C3—H3	119.8	C12—C11—C12	118.66 (12)
C3—C4—C5	120.02 (13)	C10—C11—C12	119.96 (12)
C3—C4—N1	117.60 (12)	C11—C12—C13	119.04 (14)
C5—C4—N1	122.26 (13)	C11—C12—H12	120.5
C4—C5—C6	119.71 (14)	C13—C12—H12	120.5
C4—C5—H5	120.1	C8—C13—C12	120.21 (13)
C6—C5—H5	120.1	C8—C13—H13	119.9
C1—C6—C5	119.45 (14)	C12—C13—H13	119.9
C1—C6—H6	120.3		

C6—C1—C2—C3	0.8 (2)	C8—N2—C7—N1	-173.04 (12)
C11—C1—C2—C3	-178.82 (13)	C8—N2—C7—S1	4.5 (2)
C1—C2—C3—C4	-0.2 (2)	C7—N2—C8—C9	-57.4 (2)
C2—C3—C4—C5	-0.6 (2)	C7—N2—C8—C13	126.95 (15)
C2—C3—C4—N1	-176.71 (14)	C13—C8—C9—C10	-2.3 (2)
C7—N1—C4—C3	-135.00 (15)	N2—C8—C9—C10	-177.77 (14)
C7—N1—C4—C5	49.0 (2)	C8—C9—C10—C11	1.5 (2)
C3—C4—C5—C6	0.8 (2)	C9—C10—C11—C12	0.3 (3)
N1—C4—C5—C6	176.74 (13)	C9—C10—C11—C12	-179.21 (13)
C2—C1—C6—C5	-0.6 (2)	C10—C11—C12—C13	-1.3 (2)
C11—C1—C6—C5	179.04 (12)	C12—C11—C12—C13	178.17 (12)
C4—C5—C6—C1	-0.2 (2)	C9—C8—C13—C12	1.2 (2)
C4—N1—C7—N2	178.20 (13)	N2—C8—C13—C12	176.96 (13)
C4—N1—C7—S1	0.6 (2)	C11—C12—C13—C8	0.6 (2)

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N1—H1 $\cdots$ S1 <sup>i</sup>	0.83 (2)	2.58 (2)	3.3787 (13)	159.5 (16)
N2—H2 $\cdots$ S1 <sup>i</sup>	0.85 (2)	2.50 (2)	3.3272 (13)	163.2 (18)

Symmetry codes: (i)  $-x+1, y+1/2, -z+3/2$ .

Fig. 1

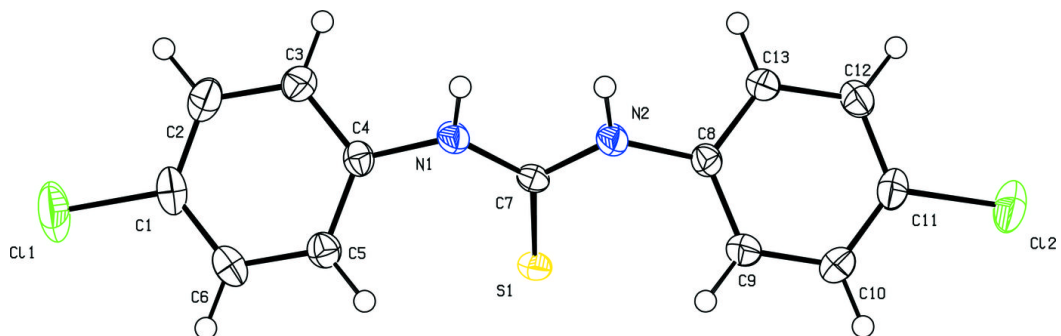




Fig. 2

