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

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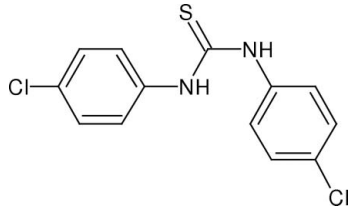
Key indicators: single-crystal X-ray study; T = 173 K; mean σ(C–C) = 0.002 Å; R factor = 0.032; wR factor = 0.083; data-to-parameter ratio = 18.1.

The structure of the title compound, $C_{13}H_{10}Cl_2N_2S$, 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 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.

Related literature

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



Experimental

Crystal data

$C_{13}H_{10}Cl_2N_2S$
M_r = 297.19
Monoclinic, $P2_1/c$
a = 13.8552 (11) Å
b = 7.1640 (4) Å
c = 14.1324 (11) Å
β = 103.290 (6)°
V = 1365.20 (17) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.61 mm^{-1}
T = 173 (2) K
0.37 × 0.34 × 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_{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^{-3}
$\Delta\rho_{min}$ = −0.48 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1···S1^{i}	0.83 (2)	2.58 (2)	3.3787 (13)	159.5 (16)
N2—H2···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*.

BN thanks the Department of Chemistry, Mangalore University, for research facilities

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

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supplementary materials

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Comment

The structure of the title compound, $C_{13}H_{10}Cl_2N_2S$, has already been determined at room temperature [Soriano-García, Chávez, Cedillo, Pérez & Hernández (2001). Anal. Sci. 17, 799–800]. However, the postitions 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 $C_{13}H_{10}Cl_2N_2S$: 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_{iso}(H) = 1.2U_{eq}(C). The H atoms bonded to N were freely refined.

Figures

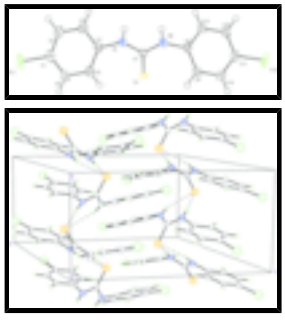

Fig. 1. Perspective view of the title compound with the atom numbering; displacement ellipsoids are at the 50% probability level.

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

Crystal data

$C_{13}H_{10}Cl_2N_2S$	F_{000} = 608
M_r = 297.19	D_x = 1.446 Mg m^{-3}

Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation $\lambda = 0.71073$ Å
Hall symbol: -P 2ybc	Cell parameters from 17612 reflections
$a = 13.8552$ (11) Å	$\theta = 3.6$–27.7°
$b = 7.1640$ (4) Å	$\mu = 0.61$ mm^{-1}
$c = 14.1324$ (11) Å	$T = 173$ (2) K
$\beta = 103.290$ (6)°	Block, colourless
$V = 1365.20$ (17) Å^3	0.37 × 0.34 × 0.32 mm
$Z = 4$	

Data collection

Stoe IPDS II two-circle diffractometer	3118 independent reflections
Radiation source: fine-focus sealed tube	2828 reflections with $I > 2\sigma(I)$
Monochromator: graphite	$R_{int} = 0.042$
$T = 173$(2) K	$\theta_{max} = 27.6^\circ$
ω scans	$\theta_{min} = 3.6^\circ$
Absorption correction: multi-scan [MULABS (Spek, 2003; Blessing, 1995)]	$h = -17 \rightarrow 17$
$T_{min} = 0.806$, $T_{max} = 0.829$	$k = -9 \rightarrow 9$
18732 measured reflections	$l = -18 \rightarrow 17$

Refinement

Refinement on F^2	Hydrogen site location: inferred from neighbouring sites
Least-squares matrix: full	H atoms treated by a mixture of independent and constrained refinement
$R[F^2 > 2\sigma(F^2)] = 0.032$	$w = 1/[\sigma^2(F_o^2) + (0.0416P)^2 + 0.5812P]$ where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.083$	$(\Delta/\sigma)_{max} = 0.001$
$S = 1.06$	$\Delta\rho_{max} = 0.43$ e Å^{-3}
3118 reflections	$\Delta\rho_{min} = -0.48$ e Å^{-3}
172 parameters	Extinction correction: SHELXL97 (Sheldrick, 1997), $Fc^* = kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Primary atom site location: structure-invariant direct methods	Extinction coefficient: 0.0115 (13)
Secondary atom site location: difference Fourier map	

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 $F^2 > 2$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 (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
Cl1	0.86710 (4)	0.20429 (9)	0.48109 (4)	0.05742 (17)
Cl2	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 (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cl1	0.0447 (3)	0.0746 (4)	0.0649 (3)	0.0117 (2)	0.0372 (2)	0.0028 (3)
Cl2	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)

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, °)

Cl1—C1	1.7502 (15)	C4—C5	1.3955 (19)
Cl2—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—Cl1	119.44 (13)	C8—C9—C10	119.78 (14)
C6—C1—Cl1	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—Cl2	118.66 (12)
C3—C4—C5	120.02 (13)	C10—C11—Cl2	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)
Cl1—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—Cl2	−179.21 (13)
C2—C1—C6—C5	−0.6 (2)	C10—C11—C12—C13	−1.3 (2)
Cl1—C1—C6—C5	179.04 (12)	Cl2—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 (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1···S1^{i}	0.83 (2)	2.58 (2)	3.3787 (13)	159.5 (16)
N2—H2···S1^{i}	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

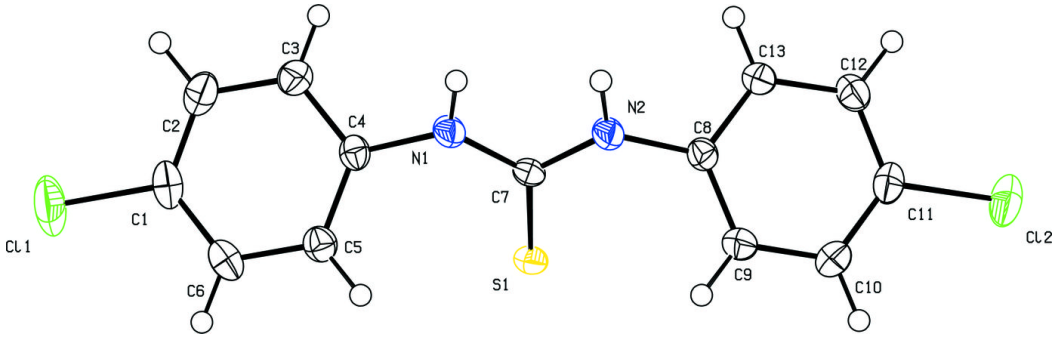

Fig. 2