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Key indicators

Single-crystal X-ray study
T = 100 K
Mean σ(C–C) = 0.003 Å
R factor = 0.028
wR factor = 0.072
Data-to-parameter ratio = 16.3

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

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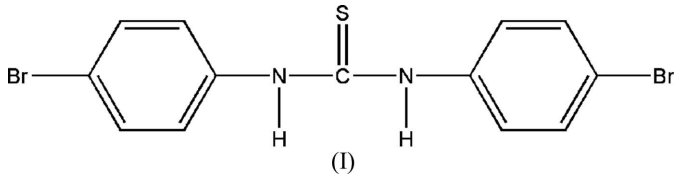
The two bromophenyl rings in the title compound, $C_{13}H_{10}Br_2N_2S$, adopt a *cis–cis* configuration to S with respect to the C—N thiourea bonds. The crystal packing is characterized by N—H···S hydrogen bonds.

Comment

N,*N*-disubstituted thiourea derivatives have attracted attention due to their coordination behavior with transition metals (Schuster *et al.*, 1990). Complexes with thiourea derivatives have also been investigated for their biological activities, such as antibacterial, antifungal, antitubercular, antithyroid and insecticidal activities (Madan & Taneja, 1991; Frech *et al.*, 1970).



(I)

The molecular structure of (I) is illustrated in Fig. 1. The short C—S distance [1.688 (2) Å] clearly shows its double-bond character. The two bromophenyl rings adopt a *cis–cis* configuration to S with respect to the C—N thiourea bonds, as observed in a homologous compound, (dichlorophenyl)thiourea (Soriano-Garcia *et al.*, 2001). The dihedral angles between the planes of the thiourea and the two bromophenyl rings (C1–C6, C8–C13) are 47.55 (10) and 52.78 (10)°, respectively. A search of the distances yielded intermolecular contacts shorter than the sum of the van der Waals radii for N and S; the units are linked by hydrogen bonds (Steiner, 1996), forming an infinite one-dimensional chain along [010] (Table 1).

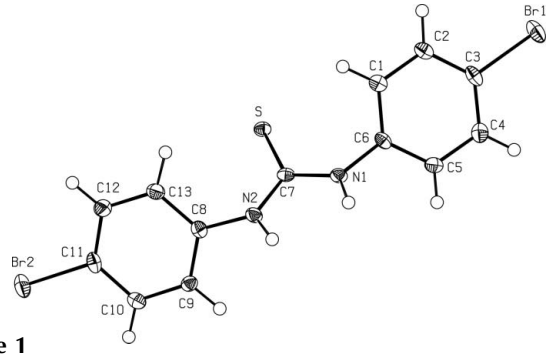


Figure 1
The molecular structure of the title compound. Displacement ellipsoids are drawn at the 50% probability level.

Experimental

A solution of 4-bromoaniline (1.72 g, 10 mmol) in acetone (20 ml) was added dropwise to a solution of CS_2 (0.90 ml, 10 mmol) and NH_3 (0.60 ml, 15 mmol) in acetone (20 ml). The mixture was stirred for about 4 h at room temperature. The solution was rotary-evaporated under vacuum. The crude product was then added to 10% HCl (200 ml) and stirred well. The solid product was separated off and recrystallized from dry acetone (yield 80%).

Crystal data

$C_{13}H_{10}Br_2N_2S$
M_r = 386.11
Monoclinic, $P2_1/c$
a = 14.077 (1) Å
b = 7.0804 (6) Å
c = 14.054 (1) Å
β = 104.026 (1)°
V = 1359.01 (18) Å^3
Z = 4
D_x = 1.887 Mg m^{-3}
Mo $K\alpha$ radiation
μ = 6.10 mm^{-1}
T = 100 (1) K
Block, colorless
0.46 × 0.42 × 0.37 mm

Data collection

Bruker SMART APEX diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2001)
T_{min} = 0.073, T_{max} = 0.106
10894 measured reflections
3318 independent reflections
2769 reflections with $I > 2\sigma(I)$
R_{int} = 0.029
θ_{max} = 28.3°

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.028
$wR(F^2)$ = 0.072
S = 1.04
3318 reflections
203 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.0404P)^2 + 0.2476P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.95 e Å^{-3}
$\Delta\rho_{min}$ = −0.42 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
N1—H21···S^{i}	0.79 (2)	2.61 (2)	3.355 (2)	158 (2)
N2—H22···S^{i}	0.79 (3)	2.53 (3)	3.316 (2)	168 (3)

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

All the H atoms were located in a difference map, and all coordinates and isotropic displacement parameters were refined.

Data collection: *SMART* (Bruker, 2001); cell refinement: *SAINT-Plus* (Bruker, 2001); data reduction: *SAINT-Plus* and *XPREP* (Bruker, 2001); program(s) used to solve structure: *SIR2004* (Burla *et al.*, 2005); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2003); software used to prepare material for publication: *PLATON*.

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References

Bruker, (2001). *SMART* (Version 5.62), *SAINT-Plus* (Version 6.02A) and *XPREP* (Version 5.1/NT). Bruker AXS Inc., Madison, Wisconsin, USA.
Burla, M. C., Caliandro, R., Camalli, M., Carrozzini, B., Cascarano, G. L., De Caro, L., Giacovazzo, C., Polidori, G. & Spagna, R. (2005). *J. Appl. Cryst.* **38**, 381–388.
Frech, F. A., Blanz, E. J., Amaral, J. R. D. & French, D. A. (1970). *J. Med. Chem.* **13**, 1117–1124.
Madan, V. K. & Taneja, A. D. (1991). *J. Indian Chem. Soc.* **68**, 471–472.
Schuster, M., Kugler, B. & Konig, K. H. (1990). *J. Anal. Chem.* **338**, 717–720.
Sheldrick, G. M. (1997). *SHELXL97*. University of Göttingen, Germany.
Sheldrick, G. M. (2001). *SADABS*. University of Göttingen, Germany.
Soriano-Garcia, M. S., Chavez, G. T., Cedillo, F. D., Perez, A. E. D. & Hernandez, G. A. (2001). *Anal. Sciences*, **17**, 799–800.
Spek, A. L. (2003). *J. Appl. Cryst.* **36**, 7–13.
Steiner, Th. (1996). *Cryst. Rev.* **6**, 1–57.

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(I)

Crystal data

$C_{13}H_{10}Br_2N_2S$
$M_r = 386.11$
Monoclinic, $P2_1/c$
Hall symbol: -P 2ybc
$a = 14.077$ (1) Å
$b = 7.0804$ (6) Å
$c = 14.054$ (1) Å
$\beta = 104.026$ (1)°
$V = 1359.01$ (18) Å^3
$Z = 4$
$F(000) = 752$

The final unit cell was obtained from the xyz centroids of 5020 reflections after integration using the SAINTPLUS software package (Bruker, 2000).
Reduced cell calculations did not indicate any higher metric lattice symmetry and examination of the finalatomic coordinates of the structure did not yield extra symmetry elements (Spek, 1988; Le Page 1987, 1988)
$D_x = 1.887$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 5020 reflections
$\theta = 2.9$–$29.4°$
$\mu = 6.10$ mm^{-1}
$T = 100$ K
Block, colorless
0.46 × 0.42 × 0.37 mm

Data collection

Bruker SMART Apex diffractometer
Radiation source: fine focus sealed Siemens Mo tube
Parallel mounted graphite monochromator
Detector resolution: 4096x4096 / 62x62 (binned 512) pixels mm^{-1}
φ and ω scans
Absorption correction: multi-scan (SADABS; Sheldrick, 2001)

$T_{min} = 0.073$, $T_{max} = 0.106$
10894 measured reflections
3318 independent reflections
2769 reflections with $I > 2\sigma(I)$
$R_{int} = 0.029$
$\theta_{max} = 28.3°$, $\theta_{min} = 3.0°$
$h = -18 \rightarrow 18$
$k = -9 \rightarrow 9$
$l = -15 \rightarrow 18$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.028$
$wR(F^2) = 0.072$
$S = 1.04$
3318 reflections
203 parameters
0 restraints
Primary atom site location: heavy-atom method

Secondary atom site location: structure-invariant direct methods
Hydrogen site location: difference Fourier map
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.0404P)^2 + 0.2476P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.95$ e Å^{-3}
$\Delta\rho_{min} = -0.42$ e Å^{-3}

Special details

Geometry. Bond distances, angles *etc*. have been calculated using the rounded fractional coordinates. All su's are estimated from the variances of the (full) variance-covariance matrix. The cell e.s.d.'s are taken into account in the estimation of distances, angles and torsion angles

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 (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
Br1	−0.36823 (2)	0.19030 (3)	0.51761 (2)	0.0285 (1)
Br2	0.46781 (2)	0.19606 (3)	0.16394 (2)	0.0269 (1)
S	0.08535 (4)	0.15939 (7)	0.39401 (4)	0.0150 (1)
N1	−0.04879 (13)	0.4225 (3)	0.31854 (13)	0.0157 (5)
N2	0.09041 (13)	0.4346 (3)	0.26553 (13)	0.0165 (5)
C1	−0.09820 (16)	0.3287 (3)	0.46781 (17)	0.0168 (6)
C2	−0.17251 (16)	0.2784 (3)	0.51259 (18)	0.0185 (6)
C3	−0.26763 (16)	0.2620 (3)	0.45654 (18)	0.0190 (6)
C4	−0.29103 (17)	0.2971 (3)	0.35681 (18)	0.0205 (6)
C5	−0.21641 (16)	0.3469 (3)	0.31242 (17)	0.0175 (6)
C6	−0.12027 (15)	0.3619 (3)	0.36726 (16)	0.0149 (6)
C7	0.04089 (14)	0.3482 (3)	0.32398 (15)	0.0138 (6)
C8	0.18026 (14)	0.3759 (3)	0.24581 (16)	0.0157 (6)
C9	0.18244 (15)	0.3507 (3)	0.14874 (16)	0.0153 (5)
C10	0.26821 (16)	0.3002 (3)	0.12420 (18)	0.0181 (6)
C11	0.35179 (15)	0.2735 (3)	0.19824 (17)	0.0185 (6)
C12	0.35166 (17)	0.2991 (3)	0.29596 (18)	0.0207 (6)
C13	0.26545 (16)	0.3522 (3)	0.31977 (17)	0.0188 (6)
H1	−0.0312 (16)	0.340 (3)	0.5055 (17)	0.008 (5)*
H2	−0.1601 (18)	0.251 (3)	0.5822 (18)	0.017 (6)*
H4	−0.356 (2)	0.286 (3)	0.319 (2)	0.028 (7)*
H5	−0.2302 (16)	0.377 (3)	0.2480 (18)	0.015 (6)*
H9	0.1236 (17)	0.374 (3)	0.1001 (17)	0.015 (6)*
H10	0.272 (2)	0.287 (4)	0.060 (2)	0.027 (7)*
H12	0.411 (2)	0.285 (3)	0.346 (2)	0.026 (7)*
H13	0.2597 (17)	0.378 (3)	0.3902 (19)	0.022 (6)*
H21	−0.0697 (16)	0.492 (3)	0.2746 (18)	0.017 (6)*
H22	0.055 (2)	0.495 (4)	0.224 (2)	0.036 (8)*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Br1	0.0248 (1)	0.0338 (2)	0.0324 (2)	−0.0052 (1)	0.0178 (1)	−0.0010 (1)
Br2	0.0177 (1)	0.0320 (1)	0.0337 (2)	0.0020 (1)	0.0117 (1)	−0.0026 (1)
S	0.0178 (2)	0.0136 (2)	0.0137 (3)	0.0010 (2)	0.0038 (2)	0.0013 (2)
N1	0.0190 (8)	0.0143 (8)	0.0146 (9)	0.0038 (7)	0.0058 (7)	0.0054 (7)

N2	0.0183 (8)	0.0165 (9)	0.0160 (10)	0.0027 (7)	0.0068 (7)	0.0046 (7)
C1	0.0208 (10)	0.0130 (9)	0.0174 (11)	−0.0002 (8)	0.0065 (9)	−0.0008 (8)
C2	0.0232 (11)	0.0163 (10)	0.0181 (12)	0.0006 (8)	0.0092 (9)	0.0001 (9)
C3	0.0210 (10)	0.0149 (9)	0.0257 (12)	−0.0003 (8)	0.0145 (9)	−0.0017 (9)
C4	0.0173 (10)	0.0212 (11)	0.0232 (12)	0.0006 (8)	0.0052 (9)	−0.0014 (9)
C5	0.0217 (10)	0.0165 (10)	0.0151 (11)	0.0027 (8)	0.0058 (9)	0.0011 (8)
C6	0.0186 (10)	0.0110 (9)	0.0176 (11)	0.0020 (8)	0.0094 (8)	−0.0009 (8)
C7	0.0184 (10)	0.0126 (9)	0.0102 (10)	−0.0016 (7)	0.0030 (8)	−0.0037 (7)
C8	0.0165 (9)	0.0128 (9)	0.0189 (11)	−0.0001 (8)	0.0065 (8)	0.0012 (8)
C9	0.0156 (9)	0.0148 (9)	0.0148 (10)	−0.0006 (8)	0.0022 (8)	0.0017 (8)
C10	0.0214 (10)	0.0178 (10)	0.0166 (12)	−0.0031 (8)	0.0077 (9)	−0.0016 (8)
C11	0.0144 (9)	0.0157 (10)	0.0274 (13)	−0.0012 (8)	0.0092 (9)	−0.0001 (9)
C12	0.0186 (10)	0.0249 (11)	0.0181 (12)	−0.0025 (8)	0.0034 (9)	0.0016 (9)
C13	0.0205 (10)	0.0209 (10)	0.0156 (11)	−0.0025 (8)	0.0055 (9)	0.0005 (9)

Geometric parameters (Å, º)

Br1—C3	1.895 (2)	C8—C13	1.394 (3)
Br2—C11	1.893 (2)	C8—C9	1.384 (3)
S—C7	1.688 (2)	C9—C10	1.381 (3)
N1—C6	1.414 (3)	C10—C11	1.382 (3)
N1—C7	1.353 (3)	C11—C12	1.386 (3)
N2—C7	1.346 (3)	C12—C13	1.387 (3)
N2—C8	1.421 (3)	C1—H1	0.97 (2)
N1—H21	0.79 (2)	C2—H2	0.97 (2)
N2—H22	0.79 (3)	C4—H4	0.94 (3)
C1—C6	1.391 (3)	C5—H5	0.90 (2)
C1—C2	1.392 (3)	C9—H9	0.95 (2)
C2—C3	1.384 (3)	C10—H10	0.92 (3)
C3—C4	1.382 (3)	C12—H12	0.96 (3)
C4—C5	1.391 (3)	C13—H13	1.03 (3)
C5—C6	1.390 (3)		
Br1···Br2^{i}	3.5362 (5)	C9···C4^{viii}	3.520 (3)
Br2···Br1^{ii}	3.5362 (5)	C9···C5^{viii}	3.570 (3)
Br2···C4^{iii}	3.729 (2)	C10···S^{ix}	3.625 (3)
Br2···C12^{iv}	3.739 (2)	C10···C3^{viii}	3.460 (3)
Br2···H4^{v}	2.95 (3)	C10···C4^{iii}	3.581 (3)
S···C1	3.239 (2)	C10···C4^{viii}	3.537 (3)
S···C13	3.265 (2)	C10···C5^{iii}	3.456 (3)
S···N2^{iii}	3.316 (2)	C11···C5^{iii}	3.555 (3)
S···C9^{vi}	3.510 (2)	C11···C4^{iii}	3.520 (3)
S···N1^{iii}	3.355 (2)	C12···Br2^{x}	3.739 (2)
S···C2^{vii}	3.472 (2)	C13···S	3.265 (2)
S···C10^{vi}	3.625 (3)	C1···H1^{xi}	2.94 (2)
S···H21^{iii}	2.61 (2)	C7···H22^{iii}	2.84 (3)
S···H22^{iii}	2.53 (3)	C7···H1	2.97 (2)
S···H2^{vii}	3.08 (2)	C7···H13	3.00 (3)

S···H13	2.91 (2)	C7···H21^{iii}	2.95 (2)
S···H1	2.83 (2)	H1···S	2.83 (2)
S···H9^{vi}	2.83 (2)	H1···C7	2.97 (2)
S···H10^{vi}	3.09 (3)	H1···C1^{xi}	2.94 (2)
N1···S^{viii}	3.355 (2)	H1···H1^{xi}	2.45 (3)
N2···S^{viii}	3.316 (2)	H2···S^{vii}	3.08 (2)
C1···S	3.239 (2)	H4···Br2^{xii}	2.95 (3)
C2···S^{vii}	3.472 (2)	H5···H21	2.35 (3)
C3···C10^{iii}	3.460 (3)	H9···H22	2.35 (4)
C4···C11^{viii}	3.520 (3)	H9···S^{ix}	2.83 (2)
C4···Br2^{viii}	3.729 (2)	H10···S^{ix}	3.09 (3)
C4···C9^{iii}	3.520 (3)	H13···S	2.91 (2)
C4···C10^{iii}	3.537 (3)	H13···C7	3.00 (3)
C4···C10^{viii}	3.581 (3)	H21···H5	2.35 (3)
C5···C10^{viii}	3.456 (3)	H21···H22	2.05 (4)
C5···C8^{iii}	3.500 (3)	H21···S^{viii}	2.61 (2)
C5···C9^{iii}	3.570 (3)	H21···C7^{viii}	2.95 (2)
C5···C11^{viii}	3.555 (3)	H22···H9	2.35 (4)
C6···C9^{viii}	3.564 (3)	H22···H21	2.05 (4)
C8···C5^{viii}	3.500 (3)	H22···S^{viii}	2.53 (3)
C9···S^{ix}	3.510 (2)	H22···C7^{viii}	2.84 (3)
C9···C6^{iii}	3.564 (3)		

C6—N1—C7	128.21 (19)	C9—C10—C11	118.9 (2)
C7—N2—C8	127.1 (2)	Br2—C11—C10	118.53 (17)
C6—N1—H21	113.2 (17)	C10—C11—C12	121.5 (2)
C7—N1—H21	116.9 (17)	Br2—C11—C12	119.92 (17)
C7—N2—H22	112 (2)	C11—C12—C13	119.1 (2)
C8—N2—H22	116 (2)	C8—C13—C12	119.9 (2)
C2—C1—C6	119.7 (2)	C2—C1—H1	120.9 (14)
C1—C2—C3	119.6 (2)	C6—C1—H1	119.4 (14)
Br1—C3—C2	119.40 (18)	C1—C2—H2	122.4 (16)
Br1—C3—C4	119.14 (18)	C3—C2—H2	118.0 (15)
C2—C3—C4	121.5 (2)	C3—C4—H4	121.1 (17)
C3—C4—C5	118.7 (2)	C5—C4—H4	120.2 (17)
C4—C5—C6	120.7 (2)	C4—C5—H5	120.4 (15)
N1—C6—C1	122.2 (2)	C6—C5—H5	118.8 (15)
N1—C6—C5	117.79 (19)	C8—C9—H9	117.5 (15)
C1—C6—C5	119.9 (2)	C10—C9—H9	121.8 (15)
N1—C7—N2	113.76 (19)	C9—C10—H10	122.2 (18)
S—C7—N1	123.37 (16)	C11—C10—H10	118.9 (18)
S—C7—N2	122.82 (16)	C11—C12—H12	120.2 (16)
N2—C8—C13	122.4 (2)	C13—C12—H12	120.6 (16)
C9—C8—C13	119.9 (2)	C8—C13—H13	116.2 (14)
N2—C8—C9	117.62 (19)	C12—C13—H13	123.9 (14)
C8—C9—C10	120.6 (2)		

C7—N1—C6—C1	49.9 (3)	C2—C3—C4—C5	1.1 (3)

C7—N1—C6—C5	−134.1 (2)	C3—C4—C5—C6	−0.3 (3)
C6—N1—C7—S	0.0 (3)	C4—C5—C6—N1	−176.8 (2)
C6—N1—C7—N2	177.7 (2)	C4—C5—C6—C1	−0.6 (3)
C8—N2—C7—S	6.1 (3)	N2—C8—C9—C10	177.7 (2)
C8—N2—C7—N1	−171.7 (2)	C13—C8—C9—C10	0.7 (3)
C7—N2—C8—C9	124.7 (2)	N2—C8—C13—C12	−178.4 (2)
C7—N2—C8—C13	−58.4 (3)	C9—C8—C13—C12	−1.5 (3)
C6—C1—C2—C3	0.0 (3)	C8—C9—C10—C11	0.6 (3)
C2—C1—C6—N1	176.8 (2)	C9—C10—C11—Br2	177.91 (16)
C2—C1—C6—C5	0.8 (3)	C9—C10—C11—C12	−1.0 (3)
C1—C2—C3—Br1	179.19 (16)	Br2—C11—C12—C13	−178.72 (16)
C1—C2—C3—C4	−0.9 (3)	C10—C11—C12—C13	0.2 (3)
Br1—C3—C4—C5	−179.05 (16)	C11—C12—C13—C8	1.1 (3)

Symmetry codes: (i) $x-1, -y+1/2, z+1/2$; (ii) $x+1, -y+1/2, z-1/2$; (iii) $-x, y-1/2, -z+1/2$; (iv) $-x+1, y-1/2, -z+1/2$; (v) $x+1, y, z$; (vi) $x, -y+1/2, z+1/2$; (vii) $-x, -y, -z+1$; (viii) $-x, y+1/2, -z+1/2$; (ix) $x, -y+1/2, z-1/2$; (x) $-x+1, y+1/2, -z+1/2$; (xi) $-x, -y+1, -z+1$; (xii) $x-1, y, z$.

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H21···S^{viii}	0.79 (2)	2.61 (2)	3.355 (2)	158 (2)
N2—H22···S^{viii}	0.79 (3)	2.53 (3)	3.316 (2)	168 (3)
C1—H1···S	0.97 (2)	2.83 (2)	3.239 (2)	106.2 (15)
C9—H9···S^{ix}	0.95 (2)	2.83 (2)	3.510 (2)	129.7 (18)

Symmetry codes: (viii) $-x, y+1/2, -z+1/2$; (ix) $x, -y+1/2, z-1/2$.