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1,3-Bis(2-chlorophenyl)thiourea

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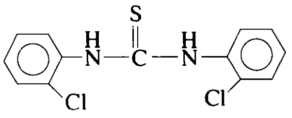
Abstract

The crystal structure determination of the title compound, $C_{13}H_{10}Cl_2N_2S$, at 173 K is reported. There are two molecules in the asymmetric unit connected by N—H···S hydrogen bonds and a short Cl···Cl contact. The molecules exist as dimers and the crystal lattice consists of two-dimensional parallel layers of these dimers connected by C—H···Cl hydrogen bonds.

Comment

Crystal structure analyses of many metal complexes of thiourea have been reported in the past, but only a few of these involve substituted thioureas and there is no structural report exclusively concerning substituted thiourea derivatives, which may be due to the difficulty in preparing crystals suitable for X-ray diffraction studies. These thiourea complexes have applications as rubber accelerators, as intermediates in dye preparation and they are also very useful agrochemical intermediates (Ramadas, Srinivasan & Janarthanan, 1993). We are interested in the molecular conformations and the N—H···S hydrogen-bond details of these molecules in the solid state. In this paper, we report the crystal structure determination of a symmetrically substituted thiourea derivative, 1,3-bis(*o*-chlorophenyl)thiourea (OCDPTU), at 173 K.



OCDPTU

A displacement ellipsoid plot of the two molecules in the asymmetric unit, together with the numbering scheme, is shown in Fig. 1. There are some notable differences in the corresponding bond angles of the two molecules, such as angle C1—N2—C8 and the angles around C1. The S1=C1 bond lengths agree well with the value observed in diphenyl thiourea (DPTU; Akilan, Sivakumar, Subramanian, Janarthanan, Ramadas & Fun, 1995) and the unweighted mean value (1.681 Å) given for C=S in thioureas (Allen, Kennard, Watson, Brammer, Orpen & Taylor, 1987). It is only in these two symmetrically substituted thiourea derivatives, OCDPTU and DPTU, that the C=S bond lengths show shorter values, whereas in other structures, C=S is observed to be more than 1.700 Å (Akilan, Sivakumar, Subramanian, Meerarani, Ramadas & Fun, 1996).

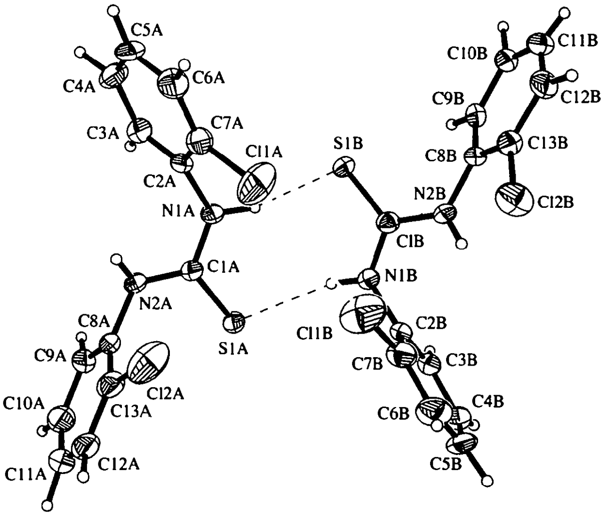


Fig. 1. Displacement ellipsoid plot of the two independent molecules in the asymmetric unit, showing the numbering scheme and ellipsoids at the 50% probability level. The N—H···S hydrogen bonds are shown as dashed lines and the Cl···Cl short contact as a dotted line.

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The dihedral angles between the plane of the thiourea moiety and the two chlorophenyl rings are 76.6 (2) and 95.5 (2)° in molecule *A*, and 95.2 (2) and 48.3 (1)° in molecule *B*. The relevant torsion angles describing the orientations are given in Table 2.

The two molecules in the asymmetric unit exist as a dimer connected by N—H···S hydrogen bonds and a short Cl···Cl interaction [N1*A*···S1*B* 3.250 (4) Å, N1*A*—H1*A*···S1*B* 163 (4)°; N1*B*···S1*A* 3.276 (4) Å, N1*B*—H1*B*···S1*A* 158 (4)°]. The short contact between atoms Cl1*A* and Cl1*B* is 3.450 (2) Å, which is less than the sum of the van der Waals radii. In the crystal lattice, the dimers are located in parallel layers perpendicular to the *c* axis (Fig. 2). There are two C—H···Cl hydrogen bonds, one connecting dimers in the same plane (C5*A*—H5*A*···Cl2*A*) and the other cross linking the dimers of adjacent planes (C6*B*—H6*B*···Cl2*A*). The details are: C5*A*···Cl2*A*^{i} 3.767 (5) Å and C5*A*—H5*A*···Cl2*A*^{i} 158 (4)°; C6*B*···Cl2*A*^{ii} 3.575 (6) Å and C6*B*—H6*B*···Cl2*A*^{ii} 152 (4)° [symmetry codes: (i) $x+1, y, z$; (ii) $x-\frac{1}{2}, \frac{1}{2}-y, 2-z$].

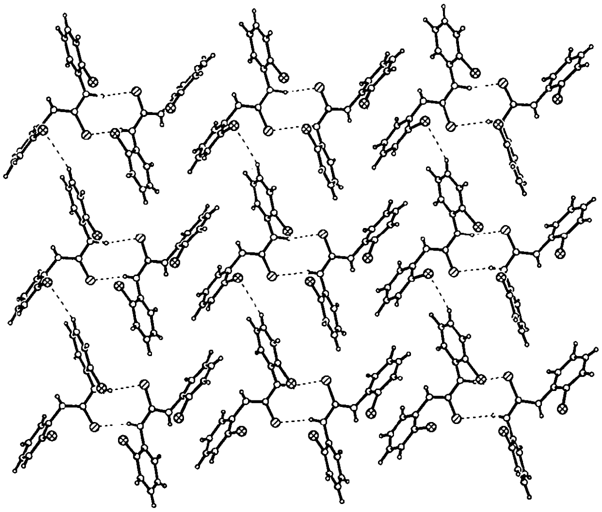

Fig. 2. One layer of OCDPTU molecules viewed down the crystallographic *c* axis.

The two chlorophenyl rings adopt a *trans–cis* configuration with respect to the thiourea moiety, as is observed in most other substituted thiourea derivatives. This is contrary to the structures of the two closest homologous compounds, DPTU and 1,3-bis(3,4-dichlorophenyl)urea (Stankovic & Andreetti, 1978), where the configuration is *cis–cis*. The *trans–cis* configuration favours dimer formation among the molecules. To our knowledge, this is the first structure among the disubstituted thiourea derivatives where the *trans* N—H group (N2—H) does not take part in any hydrogen-bond network.

Experimental

The preparation of the title compound involves a novel cost-effective synthetic procedure (Ramadas & Janarthanan, 1995). Single crystals were obtained by slow evaporation of an ethanol–hexane solution.

Crystal data

$C_{13}H_{10}Cl_2N_2S$
$M_r = 297.19$
Orthorhombic
$P2_12_12_1$
$a = 9.451$ (3) Å
$b = 11.916$ (2) Å
$c = 23.938$ (7) Å
$V = 2695.9$ (12) Å^3
$Z = 8$
$D_x = 1.464$ Mg m^{-3}

Mo *Kα* radiation
$\lambda = 0.71073$ Å
Cell parameters from 30 reflections
$\theta = 10$–25°
$\mu = 0.618$ mm^{-1}
$T = 173$ (2) K
Needle
0.60 × 0.26 × 0.12 mm
Colourless

Data collection

Siemens *P*4 diffractometer
$\theta/2\theta$ scans
Absorption correction: none
6075 measured reflections
4734 independent reflections
3742 observed reflections [$I > 2\sigma(I)$]
$R_{int} = 0.0449$

$\theta_{max} = 25.03°$
$h = -1 \rightarrow 11$
$k = -14 \rightarrow 13$
$l = -28 \rightarrow 6$
3 standard reflections monitored every 100 reflections intensity decay: <4%

Refinement

Refinement on F^2
$R(F) = 0.0449$
$wR(F^2) = 0.1162$
$S = 0.964$
4734 reflections
405 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.0656P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = -0.001$

$\Delta\rho_{max} = 0.380$ e Å^{-3}
$\Delta\rho_{min} = -0.320$ e Å^{-3}
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)
Absolute configuration: Flack (1983) parameter = −0.04 (8)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$$U_{eq} = (1/3)\Sigma_i\Sigma_jU_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	*y*	*z*	U_{eq}
Cl1*A*	1.0102 (2)	0.18908 (13)	0.94188 (6)	0.0675 (4)
Cl2*A*	0.7093 (2)	0.45662 (13)	0.94373 (6)	0.0661 (4)
S1*A*	0.69876 (10)	0.28290 (8)	0.79419 (5)	0.0333 (2)
N1*A*	0.9662 (3)	0.2671 (3)	0.82517 (15)	0.0306 (7)
N2*A*	0.8647 (4)	0.4411 (3)	0.8357 (2)	0.0315 (8)
C1*A*	0.8514 (4)	0.3338 (3)	0.8200 (2)	0.0271 (9)
C2*A*	1.0993 (4)	0.2969 (3)	0.8492 (2)	0.0271 (9)
C3*A*	1.2005 (5)	0.3524 (4)	0.8184 (2)	0.0347 (10)
C4*A*	1.3351 (5)	0.3697 (4)	0.8394 (2)	0.0415 (11)
C5*A*	1.3679 (5)	0.3308 (4)	0.8920 (2)	0.0428 (12)
C6*A*	1.2688 (5)	0.2771 (4)	0.9234 (2)	0.0437 (12)
C7*A*	1.1345 (5)	0.2589 (3)	0.9023 (2)	0.0340 (10)
C8*A*	0.7481 (4)	0.5180 (3)	0.8366 (2)	0.0298 (9)
C9*A*	0.7155 (5)	0.5788 (4)	0.7889 (2)	0.0361 (10)
C10*A*	0.5993 (5)	0.6509 (4)	0.7899 (3)	0.0538 (15)
C11*A*	0.5213 (6)	0.6643 (4)	0.8366 (3)	0.0556 (15)
C12*A*	0.5555 (5)	0.6076 (4)	0.8851 (3)	0.055 (2)
C13*A*	0.6702 (5)	0.5337 (4)	0.8845 (2)	0.0378 (10)

Cl1*B*	0.6749 (2)	0.07701 (14)	0.95369 (6)	0.0738 (5)
Cl2*B*	0.82194 (14)	−0.22292 (11)	0.97865 (5)	0.0513 (3)
S1*B*	0.98095 (10)	−0.00257 (8)	0.80560 (5)	0.0315 (2)
N1*B*	0.7120 (3)	0.0188 (3)	0.8319 (2)	0.0304 (8)
N2*B*	0.8133 (4)	−0.1454 (3)	0.86052 (15)	0.0300 (8)
C1*B*	0.8278 (4)	−0.0460 (3)	0.8347 (2)	0.0262 (8)
C2*B*	0.5772 (4)	−0.0061 (3)	0.8558 (2)	0.0286 (9)
C3*B*	0.4718 (4)	−0.0506 (3)	0.8232 (2)	0.0311 (9)
C4*B*	0.3381 (5)	−0.0695 (4)	0.8454 (2)	0.0420 (12)
C5*B*	0.3090 (5)	−0.0447 (4)	0.8998 (2)	0.0465 (12)
C6*B*	0.4133 (6)	−0.0016 (5)	0.9325 (2)	0.0496 (13)
C7*B*	0.5477 (5)	0.0203 (4)	0.9115 (2)	0.0387 (11)
C8*B*	0.9220 (4)	−0.2248 (3)	0.8722 (2)	0.0266 (8)
C9*B*	1.0098 (4)	−0.2657 (3)	0.8304 (2)	0.0304 (9)
C10*B*	1.1133 (5)	−0.3449 (3)	0.8431 (2)	0.0362 (11)
C11*B*	1.1255 (5)	−0.3852 (4)	0.8970 (2)	0.0400 (12)
C12*B*	1.0375 (5)	−0.3485 (4)	0.9384 (2)	0.0379 (10)
C13*B*	0.9345 (4)	−0.2676 (4)	0.9259 (2)	0.0315 (9)

Table 2. *Comparison of selected geometry (Å, °) of the two molecules of OCDPTU*

	Molecule *A*	Molecule *B*
Cl1—C7	1.724 (4)	1.710 (5)
Cl2—C13	1.728 (5)	1.734 (4)
S1—C1	1.682 (4)	1.687 (4)
N1—C1	1.351 (5)	1.342 (5)
N1—C2	1.428 (5)	1.428 (5)
N2—C1	1.339 (5)	1.343 (5)
N2—C8	1.433 (5)	1.424 (5)
C1—N1—C2	126.7 (3)	126.0 (3)
C1—N2—C8	122.8 (3)	127.0 (3)
N2—C1—N1	117.4 (3)	116.6 (4)
N2—C1—S1	121.9 (3)	120.1 (3)
N1—C1—S1	120.7 (3)	123.2 (3)
C3—C2—N1	121.1 (4)	120.0 (4)
C7—C2—N1	119.9 (4)	120.9 (4)
C2—C7—Cl1	119.8 (3)	120.8 (3)
C13—C8—N2	120.7 (4)	121.6 (4)
C9—C8—N2	119.6 (4)	119.1 (4)
C8—C13—Cl2	119.8 (3)	120.6 (3)
C12—C13—Cl2	119.6 (4)	118.8 (3)
C2—N1—C1—S1	−176.1 (3)	−178.3 (3)
C8—N2—C1—S1	5.7 (6)	5.8 (5)
C1—N1—C2—C3	−83.1 (5)	−98.6 (5)
C1—N2—C8—C9	−88.3 (5)	−54.1 (6)

The intensity data for the title compound were collected at 173 K using a Siemens LT-2 attachment since there was large peak broadening at room temperature. The structure was solved by direct methods and refined by the full-matrix least-squares technique. All the H atoms were located from difference maps and refined isotropically. *PARST* (Nardelli, 1983) was used for geometric calculations.

Data collection: *XSCANS* (Siemens, 1994). Cell refinement: *XSCANS*. Data reduction: *XSCANS*. Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990*a*). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *SHELXTL/PC* (Sheldrick, 1990*b*). Software used to prepare material for publication: *SHELXL*93.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: AS1197). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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N-[3-Methyl-2(3*H*)-thiazolylidene]benzamide Containing a Short Intramolecular S···O Contact

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Abstract

The title molecule, $C_{11}H_{10}N_2OS$, shows a short intramolecular S···O contact of 2.622 (1) Å, *ca* 0.6 Å less than the sum of the traditional van der Waals radii. Electrostatic attraction, due to charge delocalization from the heterocycle into the carbonyl group, contributes to this short interaction.

Comment

The van der Waals radii of atoms (Bondi, 1964) are not always a good guide for estimating minimum inter- and intramolecular contact distances. It is necessary to consider any effects producing attractive interactions, such as HOMO/LUMO interactions (Bürgi, Dunitz & Schefter, 1973) and cooperative interactions, and to allow for the asymmetric shape of certain bonded atoms (Nyberg & Faerman, 1985). The two latter factors contribute to the short intramolecular S···S contact in