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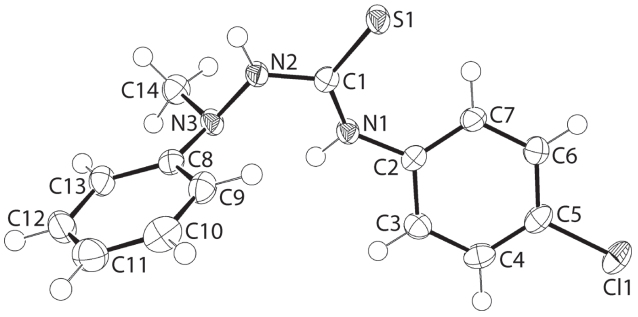
Crystal structure of 1-(4-chlorophenyl)-3-[methyl (phenyl)amino]thiourea, $C_{14}H_{14}ClN_3S$



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Abstract

$C_{14}H_{14}ClN_3S$, orthorhombic, *Pbca* (no. 61), $a = 10.4000(2)$ Å, $b = 11.5622(2)$ Å, $c = 23.4776(4)$ Å, $V = 2823.11(9)$ Å^3, $Z = 8$, $R_{gt}(F) = 0.0284$, $wR_{ref}(F^2) = 0.0774$, $T = 100(2)$ K.

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Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

Table 1: Data collection and handling.

Crystal:	Colourless prism
Size:	$0.13 \times 0.05 \times 0.04$ mm
Wavelength:	Cu $K\alpha$ radiation (1.54184 Å)
μ:	3.68 mm^{-1}
Diffractometer, scan mode:	XtaLAB Synergy, ω
θ_{max}, completeness:	67.1°, >99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	17794, 2528, 0.032
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 2339
$N(param)_{refined}$:	179
Programs:	CrysAlis^{PRO} [1], SHELX [2, 3], WinGX/ORTEP [4]

Source of material

4-Chlorophenyl isothiocyanate (Sigma Aldrich; 1.69 g, 0.01 mol) in acetonitrile (10 mL) was added dropwise to an equivalent molar amount of 1-methyl-1-phenylhydrazine (Merck; 1.18 mL, 0.01 mol) in acetonitrile (10 mL). The mixture was stirred for 2 h after which chloroform (20 mL) was added. The solution was left for evaporation at room temperature, yielding colourless crystals after 2 weeks. *M*.pt (Biobase melting point apparatus MP450): 442–443 K. Elem. Anal. (Leco TruSpec): Calc. for $C_{14}H_{14}ClN_3S$: C, 57.63; H, 4.84; N, 14.40%. Found: C, 57.53; H, 5.07; N, 14.27%. **^{1}H NMR** (Bruker Ascend 400 MHz spectrometer, shifts relative to Me_4Si; $CDCl_3$): δ [p.p.m.] 8.84 (s, br, 1H, Ph—NH), 7.70 (s, br, 1H, N—NH), 7.53 (d, 2H, NC_6H_4Cl-3,5, $^3J_{HH} = 8.72$ Hz), 7.37–7.32 (m, 2H, NC_6H_5-3,5), 7.30 (d, 2H, NC_6H_4Cl-2,6, $^3J_{HH} = 8.76$ Hz), 7.05 (t, 1H, NC_6H_5-4, $^3J_{HH} = 7.38$ Hz), 7.00 (d, 2H, NC_6H_5-2,6, $^3J_{HH} = 7.91$ Hz), 3.21 (s, 3H, NCH_3). **^{13}C{^{1}H} NMR** (Bruker Ascend 400 MHz spectrometer; $CDCl_3$): δ [p.p.m.] 180.0 (Cq), 148.7 (NC_6H_5, C1), 136.2 (NC_6H_4Cl, C1), 131.4 (NC_6H_4Cl, C4), 129.6 (NC_6H_4Cl, C3, C5), 128.8 (NC_6H_4Cl, C2, C6), 125.6 (NC_6H_5, C3, C5), 122.6 (NC_6H_5, C4), 114.9 (NC_6H_5, C2, C6), 42.0 (NCH_3). **IR** (Bruker Vertex 70v spectrophotometer, cm^{-1}): 3264 (*m*) ν(N—H), 1488 (s) ν(C—N), 1255 (s) ν(C=S).

Experimental details

The C-bound H atoms were geometrically placed (C—H = 0.95–0.98 Å) and refined as riding with $U_{iso}(H) = 1.2$–$1.5U_{eq}(C)$. The N-bound H atoms were located in a difference Fourier map but were refined with a distance restraint of N—H = 0.88 ± 0.01 Å, and with $U_{iso}(H)$ set to $1.2U_{equiv}(N)$.

Comment

Recent structural studies of molecules of the general formula Me(*R*)NN(H)C(=S)N(H)(PhY-4) have revealed a high degree of homogeneity in terms of the adopted molecular geometry and in the formation of supramolecular synthons of the type $\{\cdots HNCS\}_2$ owing to the *syn* disposition of the thione-S and thioamide-N—H atoms [5, 6]. The main motivations for investigating such di-substituted thiourea derivatives comes about owing to their utility in asymmetric synthesis as dual hydrogen bonding catalysis [7] and their pharmaceutical potential [8].

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Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2).

Atom	*x*	*y*	*z*	U_{iso}*/U_{eq}
Cl1	1.10565(4)	0.53817(4)	0.22483(2)	0.03176(13)
S1	0.65724(3)	0.44069(3)	0.44029(2)	0.01886(12)
N1	0.73050(11)	0.65576(10)	0.40536(5)	0.0156(2)
H1N	0.7099(16)	0.7287(9)	0.4054(7)	0.019*
N2	0.55180(11)	0.64007(10)	0.46063(5)	0.0170(3)
H2N	0.5015(14)	0.6021(14)	0.4843(6)	0.020*
N3	0.53154(11)	0.76010(10)	0.45575(5)	0.0164(2)
C1	0.64935(13)	0.58614(13)	0.43432(6)	0.0150(3)
C2	0.82739(12)	0.62659(12)	0.36539(6)	0.0149(3)
C3	0.85227(13)	0.70651(12)	0.32236(6)	0.0188(3)
H3	0.8088	0.7788	0.3222	0.023*
C4	0.93989(14)	0.68124(13)	0.27983(6)	0.0217(3)
H4	0.9571	0.7359	0.2506	0.026*
C5	1.00250(14)	0.57522(14)	0.28030(6)	0.0205(3)
C6	0.98471(14)	0.49808(13)	0.32446(6)	0.0203(3)
H6	1.0316	0.4276	0.3254	0.024*
C7	0.89759(13)	0.52412(13)	0.36765(6)	0.0183(3)
H7	0.8861	0.4721	0.3986	0.022*
C8	0.41299(13)	0.78552(12)	0.42717(6)	0.0162(3)
C9	0.37541(14)	0.71855(13)	0.38050(6)	0.0205(3)
H9	0.4257	0.6538	0.3694	0.025*
C10	0.26488(15)	0.74629(15)	0.35031(7)	0.0266(3)
H10	0.2393	0.6996	0.3190	0.032*
C11	0.19132(15)	0.84168(15)	0.36549(7)	0.0281(4)
H11	0.1166	0.8613	0.3443	0.034*
C12	0.22811(14)	0.90769(13)	0.41173(7)	0.0253(3)
H12	0.1782	0.9731	0.4222	0.030*
C13	0.33736(14)	0.87961(13)	0.44315(6)	0.0197(3)
H13	0.3603	0.9246	0.4755	0.024*
C14	0.55625(14)	0.81815(12)	0.51024(6)	0.0214(3)
H14A	0.4890	0.7972	0.5376	0.032*
H14B	0.5560	0.9021	0.5045	0.032*
H14C	0.6402	0.7939	0.5250	0.032*

The molecule is shown in the figure (70% displacement ellipsoids) and is constructed about a planar chromophore with the r.m.s. deviation of the C1, N1, N2 and S1 atoms being 0.0015 Å. This planarity does not extend to the N3 [0.078(2) Å] and, especially, C2 [0.236(2) Å] atoms, each of which lie to the same side of the central plane. The terminal phenyl rings are inclined with respect to the central plane with the dihedral angles between the latter and the N1- and N3-bound phenyl rings being 27.01(7) and 82.50(4)°, respectively. The twist in the molecule is confirmed by the dihedral angle between the phenyl rings of 71.07(4)°. As for the literature structures [5, 6], the amine-H atoms lie to opposite sides of the central plane, a configuration enabling the formation of an intramolecular hydrogen bond [H1n$\cdots$N3 = 2.229(16) Å, N1$\cdots$N3 = 2.6714(16) Å with angle 111.3(12)°] to close a loop.

Again consistent with literature precedents, centrosymmetrically related molecules are connected by an eight-membered $\{\cdots HNCS\}_2$ synthon as the result of the formation of amine-N2—*H*$\cdots$S1(thione) hydrogen bonds [N2—H2n$\cdots$S1^{i}: H2n$\cdots$S1^{i} = 2.471(14) Å, N2$\cdots$S1^{i} = 3.3180(12) Å with angle 161.6(14)° for i = $1-x$, $1-y$, $1-z$]. The dimeric aggregates are three-dimensionally connected by phenyl- and methyl-C-π(phenyl-C8—C13) interactions [C6—H6$\cdots$*Cg*(C8—C13)^{ii} = 2.74 Å with angle 139°, and C14—H14*c*$\cdots$*Cg*(C8—C13)^{iii} = 2.59 Å with angle 154° for ii: $3/2-x$, $-1/2+y$, z and iii: $1/2+x$, $3/2-y$, $1-z$] as well as C5—Cl1$\cdots$π(phenyl-C2—C7) interactions [C5—Cl1$\cdots$*Cg*1(C2—C7)^{iv} = 3.5119(7) Å with angle at Cl1 = 139.30(5)° for iv: $1/2+x$, y, $1/2-z$].

The structure of the present compound is isostructural with the 4-Me analogue [6]. As anticipated, equivalent intermolecular interactions are present in both crystals with the additional C5—Cl1$\cdots$π(phenyl-C2—C7) contact obviously lacking in the 4-Me structure. Despite the formation of the latter contact in the title compound, structural mimicry is still obtained in this pair of structures where the only difference is a chloro/methyl exchange [9]. This observation suggests the C5—Cl1$\cdots$π(phenyl-C2—C7) contact may arise as a result of global molecular packing rather than being structure directing.

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